

TRITIUM PENETRATION THROUGH CONCRETE

FINAL REPORT

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SUMMARY

The isolation of tritium-bearing water in low-level waste repositories, such as near surface vaults, may be a major environmental problem. Tracer tests have been conducted to determine the penetration of tritiated water through concrete samples representing formulations selected for vault construction. Of the proposed migration processes, pore migration, hydrogen exchange in water of crystallization and vapor diffusion, the pore migration process in wetted concrete was found to dominate so strongly, that the others, if present, could not be identified.

Migration tests were done on 6-inch diameter concrete specimens, 2 - 8 inches (5 - 20 cm) long both under gravity alone and with a 50 and 100 cm hydrostatic head. Migration through the thinner specimens was very rapid, about 1 - 7 cm per day depending on porosity. For the longer columns, infiltration rates varied slightly with pressure, but stabilized in the range of $0.8 - 5 \times 10^{-3}$ ml/cm²-day or about 4×10^{-3} cm/day. A concrete formulation using a smaller size aggregate, No. 8 stone, showed slightly lower migration rates.

It would appear that little credit can be taken for retardation of tritium movement by the vault walls once the concrete walls have been thoroughly wetted.

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INTRODUCTION

Cement and concrete are widely used in low-level waste management both as a means of solidifying waste and for containment of dry or liquid wastes. Concrete technology is well-established and goes back for centuries (e.g. Langton) and a large number of reports have been published on the mechanical performance and leachability of concrete waste forms (see References at end for examples). Structurally concrete is strong in compression, but it is inherently a porous material and permeable to water, unless specially treated or coated, as most homeowners know. Unless it is reinforced, it is liable to crack when stressed, but such cracks may be of limited length owing to the heterogeneous nature of the concrete mixture. Typical "concrete" is a mixture of cement, sand, stone aggregate and water in various proportions, that together determine the structural properties and tightness of the poured material. Water content is one of the critical parameters and must be carefully controlled during pouring and setting; to a large extent it will determine the porosity of the resulting material.

Tritium, hydrogen-3, is a major component in many low-level radioactive wastes and its containment may pose some special problems, because of its ready exchange and equilibration with environmental hydrogen and the ubiquity of hydrogen, even though the internal dose effects from tritium intake in animals and humans are relatively low. One of the areas of interest in the present project is the storage of "saltstone", solidified nitrate waste material, in concrete vaults. In order to estimate the degree of retention of tritium in aqueous form in such vaults, it was considered necessary to measure tritium migration through the concrete wall material and that was the objective of the present study.

Cement is a porous, continuously hydrating material whose actual surface area greatly exceeds its geometric surface area. In leaching, the rates of dissolution vary as a function of phase chemistry and this dissolution exposes or enlarges pores; thus the leaching behavior must be related to pore structure and the composition of the pore solution (Hoyle). Cement is a multiphasic material described by phase relations in the quaternary system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$, with various oxide impurities. Sand and aggregate act as fillers and grain boundary interlocks and much of the migration mechanism in concrete depends on the interfaces between these materials and on the relative ease of diffusion of water molecules along such boundaries as against bulk flow through pores and cracks.

The water chemistry of concrete is fairly complicated. Hydration of cement involves a number of reactions that result in a variety of hydrides and hydroxides as well as some free water of crystallization. In addition, the reactions of blending agents, such as fly ash, slag or silica fume, with Ca(OH)_2 result in secondary reactions leading to various hydroxides and sulfhydrides (e.g. Berner). The cement pore waters then contain a variety of soluble alkali hydroxides and some sulfates. Glasser *et al.* have also described the behavior of calcium silicate hydrate (C-S-H) gels in cements. Such studies, however, have more of a bearing on the migration or retention of dissolved cations or anions than of water itself.

Atkinson and Hearne have discussed the reactions of concrete with the aqueous environment. Principally, exposure of concrete to water leads to leaching out of Ca(OH)_2 from the concrete phases. The loss of Ca results in a loss of strength, about 1.5% loss for every 1% loss of total Ca. Long-term removal of Ca, first as free Ca(OH)_2 , then from the C-S-H gel, may result in eventual collapse of the structure. Other disruptive effects may arise from the presence of Mg SO_4 or CaSO_4 in the water.

Atkinson and Hearne also point out the susceptibility of the cement phase in concrete to changes in relative humidity. Pronounced wet/dry cycling may lead to dehydration of hydrated compounds and dimensional changes, resulting in crack formation. For that reason, once concrete has been placed, it should be maintained in a condition of high humidity to minimize cracking and degradation. This implies keeping the material fairly wet, i.e. maintaining the pores filled with water. This leads to a gradual lowering of the pH in pore water with time from pH 13 to 12 and ultimately lower, but over a vastly longer time scale than would be of concern for tritium with its 12.3 year half life (Ewart).

To predict the containment of tritium by a concrete barrier one needs to consider all possible pathways. Assuming that the source of tritium is in the form of tritiated water, HTO, one can postulate several pathways:

1. Movement of pore water through cracks and pores in the concrete.
2. Tritium exchange with hydrogen in the hydrated cement components.
3. Vapor movement as HT through open pores or cracks.
4. Diffusion of dissociated H^+ ions or HT molecules through the concrete crystal structure, and
5. A combination of pore movement and diffusion of HTO through pore-boundary materials under barometric or hydrostatic pressures.

Unless the concrete has dried out fully, by exposure to dry, warm conditions, both vapor movement and diffusion of ions would be expected to be greatly overshadowed by actual water movement. Because of the complexity of the concrete formation process, the properties of the final product are very dependent on pouring temperature, water losses and trapped air and any pressing or working of the slurry during the pouring process. Neville quotes variations in vapor permeability ranging from 8×10^{-12} to 28×10^{-12} m/s as the water-cement ratio varies from 0.69 to 0.46 at 23°C. Rogers *et al.*

present oxygen diffusion rates through 7 cm of saturated cement ranging from 3.5 to 6.3×10^{-8} mg/cm² sec as water-cement ratios go from 0.40 to 0.60. In all cases the permeability parallels the capillary porosity.

Gause *et al.* asserted that transport of tritiated liquid through concrete will occur by diffusion. Diffusion of tritiated liquids would be slow if the pores are filled with liquid, but faster through the gas phase, and they conclude that "in the long term, concrete cannot be relied upon as a containment barrier for the tritiated solvents". For gaseous diffusion, they estimate a diffusion coefficient for tritium in cement of about 1×10^{-2} cm²/sec, implying very rapid transport of tritium gas through a cement waste overpack. For diffusion of tritiated water in concrete, Gause *et al.* quote values in the range of 10^{-8} - 10^{-9} cm²/sec, much slower than for gaseous transport.

Matsuzuru *et al.* show comparable porosities for Portland-cement composites and slag-cement composites. Porosities in both cases varied from 25 - 38 volume percent as the water-cement ratio was varied from 33 to 45 weight percent. Observations in the present work also confirm increasing porosity in surface layers as air and moisture are expelled from internal volumes by weight and compaction. Liquid diffusion rates in concrete of the order of 10^{-9} cm²/sec have also been reported for cesium migration in water by several investigators.

Under normal conditions, with the waste in dry, solidified form, no migration of tritium from the waste form should be anticipated. However, as a conservative assumption to estimate leakage under worst case conditions, water infiltration due to failure of the top cap must be assumed. Under those conditions there may be some standing water in the vault, leading to limited leaching and movement of tritium into that water and setting up a hydrostatic pressure head across the walls.

The purpose of the present investigation was to measure directly the mobility of tritiated water through concrete specimens representative of the material proposed for waste storage vaults at the Savannah River Plant, using tritiated water as the radiotracer and simulating worst-case conditions.

EXPERIMENTAL DETAILS

The basic experimental procedure involved the following steps:

1. Preparation of concrete specimens
2. Preparation of tritiated water samples
3. Soaking of specimens in water
4. Column set up
5. Application of hydrostatic pressure, where needed
6. Sampling of effluents
7. Tritium profile determination in some cases
8. Waste disposal

Materials

Concrete samples were prepared according to the SRP Saltstone vault specifications:

1. Compression strength greater than 4000 psi at 91 days
2. Slump no greater than 3 inches
3. Composition

Portland cement, type II	350 lb/cu. yd
Grade 120 slag	233
Sand	1280
No. 67 stone	1774
Water	271
Water reducing admixture	24 oz/cu.yd.

Cylindrical samples, 6 inches in diameter were prepared in the Georgia Tech Geotechnical and Materials Laboratory.

For some later runs, equal proportions of No. 8 stone were substituted for No. 67. The slag material was provided by Savannah River Laboratory.

Vibrating compaction of the aggregate was employed on the last set of test specimens prepared and seemed to result in a somewhat lower porosity (see last entries in Table 3, p. 44).

Specimen cylinders were sawed into slices nominally 2, 4, 6 and 8 inches in length after trimming off rough end pieces and removing any obviously cracked material.

Characterization of concrete material

A. Particle-size distribution of aggregate

Method: ASTM D422-63 (1972)
"Particle-size analysis of Soil"

Figure 1 presents a conventional particle size analysis for the concrete material, after screening out the #67 stone.

B. Porosity:

Method: ASTM C20-83
"Standard test methods for apparent porosity, water absorption, apparent specific gravity, and bulk density of burned refractory brick and shapes by boiling water".

Procedure:

1. Dry the test specimens to constant weight in 105 - 110°C and determine the dry weight (D).
2. Place the test specimens in boiling water for 2 hours. During the boiling period, keep them entirely covered with water, and allow no contact with the heated bottom of the container.
3. After boiling, keep the specimens immersed in room-temp. water for a minimum of 12 hr.
4. Determine the suspended weight(S) after boiling and while suspended in water, suspending the specimen in a loop of copper while hung from one arm of the balance.
5. After determining the suspended weight, perform the blotting operation by rolling the specimen lightly on the wet cloth, and then press only enough to remove such water as will drip from the cloth.
6. Determine the saturated weight (W) of the specimen by weighing in air.

Data:

Dry Weight D =	1804.35 g
Suspended Weight S =	1073.36 g
Saturated Weight W =	1873.55 g

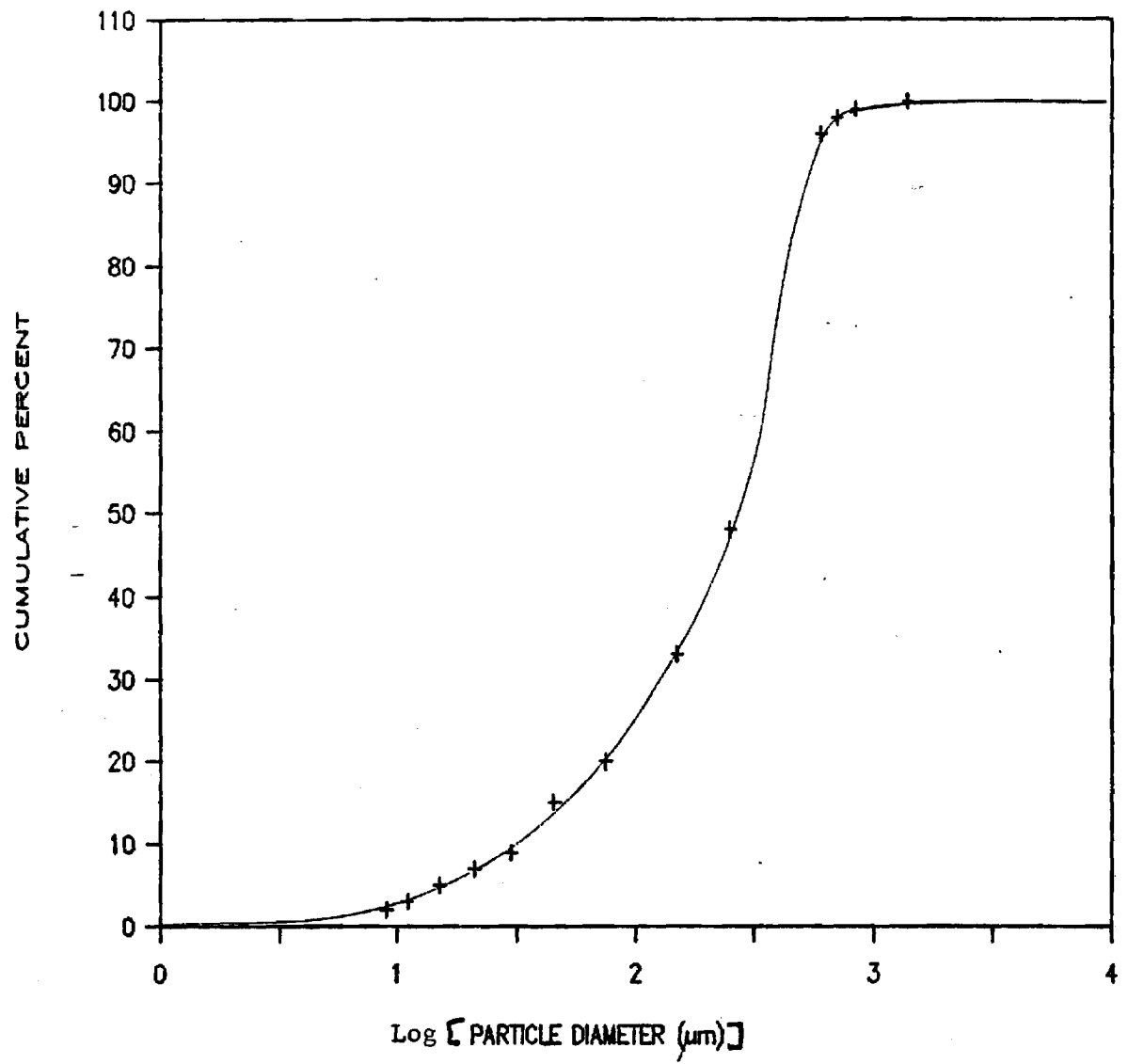


Fig. 1. Particle size analysis of pulverized concrete.

Results: (Assume that ρ water = 1 at normal temp.)

Exterior Volume

$$V_{ex} = W - S = 800.19 \text{ cm}^3$$

Volume of open pore

$$V_{op} = W - D = 68.7 \text{ cm}^3$$

Apparent porosity

$$p = V_{op}/V_{ex} = 8.59\%$$

Water Absorption

A = the wt. of water absorbed/wt. of dry specimen

$$= [(W-D)/D] \times 100 = 3.81\%$$

Bulk density

$$= D/V_{ex}$$

$$= 1804.35 \text{ g}/800.19 \text{ cm}^3 = 2.26 \text{ g/cm}^3$$

(NB) This bulk density is almost the same as the original value derived from concrete mix ($\sim 2.24 \text{ g/cm}^3$)

$$\begin{aligned} \text{Unit wt.} &= 152.5 \text{ lb/ft}^3 \text{ (from C. E. Department concrete mix design)} \\ &= 2.44 \text{ g/cm}^3 \text{ (containing water)} \end{aligned}$$

$$\begin{aligned} \text{Unit wt.} &= 2.44 \text{ g/cm}^3 \times \frac{112 \text{ lb water excluding}}{122 \text{ lb total mix wt.}} \\ \text{(100\% dry water)} & \end{aligned}$$

$$= \underline{2.24 \text{ g/cm}^3}$$

* only some portion of water is used to fix concrete particles to each other. The remainder will be evaporated as it becomes dry.

Experimental System

Since the experimental samples were largely composed of two types of sample, i.e., rectangular-shape samples and cylindrical ones, the experimental system had to fit these and the purpose of the experiment.

Experimental systems were divided into one-time source input systems and continuous source-input systems. One-time source input system means that tritiated water would be added onto the top with the same source density over the whole top surface, as an input pulse, and remain in the sample until it reached the bottom water in a 100 - 500 ml beaker. This pulse source input method was applied only to the rectangular concrete samples. In order to avoid evaporation to the outside, plastic wrap material was used to cover the whole system.

For the larger cylindrical samples, deionized water was used at an early stage to check the infiltration rate by means of a gravimetric method in which water was taken out above a fixed water level. As time went by, the flow rate became very slow and it became impossible to detect further infiltration. Therefore, in most cases a tracer method with tritiated water was applied to estimate the infiltration rate. A Lucite tube, 6" in diameter, was used to contain the heavy concrete sample. The top cover had an O-ring to provide a seal for pressurizing the experiment. In order to avoid any side flow through and along the outer surface of the concrete sample, a plaster material was used, as well as absorbent paper rings. A pipe was inserted at the top of the system to apply the pressure to simulate the standing water over the top of the concrete layer. (Fig. 2)

The dimensions of the Lucite tube shown in the attached pictures (Figs. 2-5) were as follows:

Inside diameter	= 6" (15 cm)
Outside diameter	= 6 5/8" (17 cm)
Height	= 1 ft (30 cm)

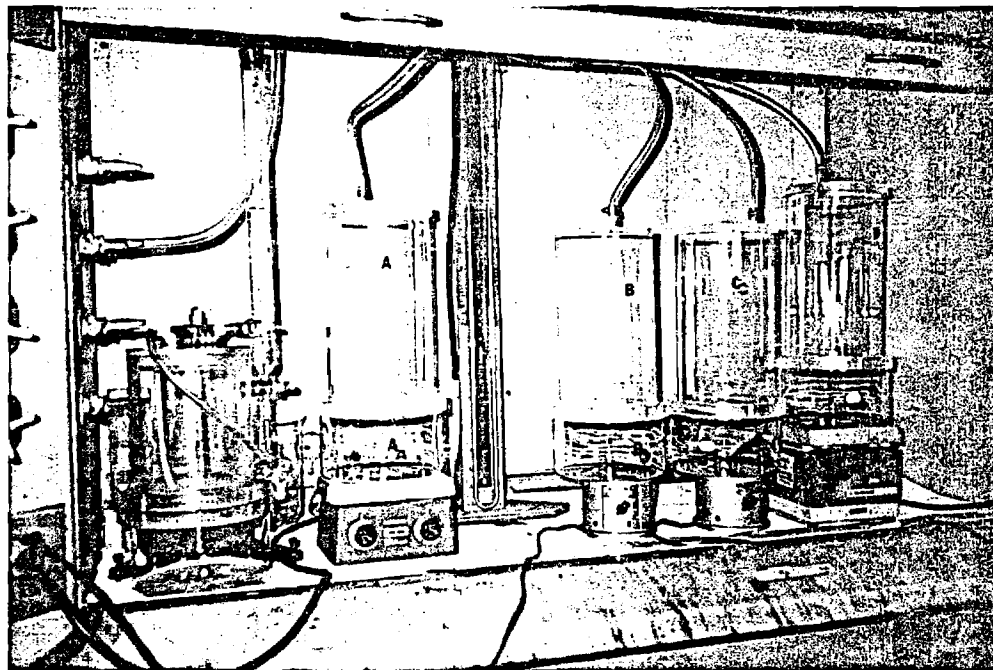


Fig. 2. Experimental set-up with container tubes under air pressure.

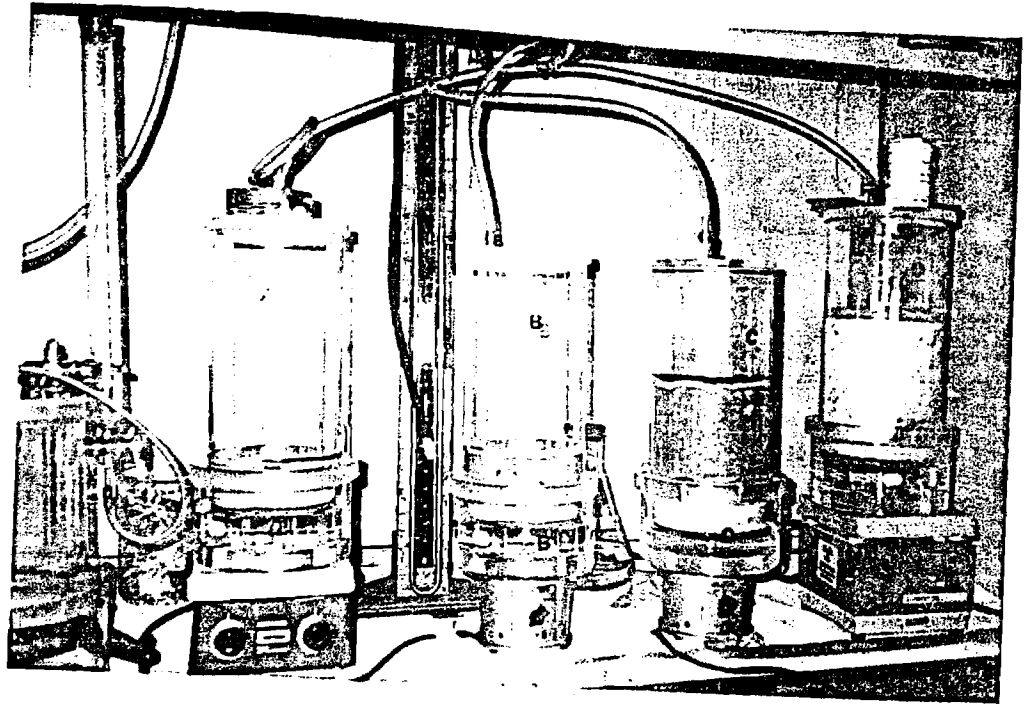


Fig. 3. Details of experimental set-up. Lucite containers holding specimens of varying thickness.

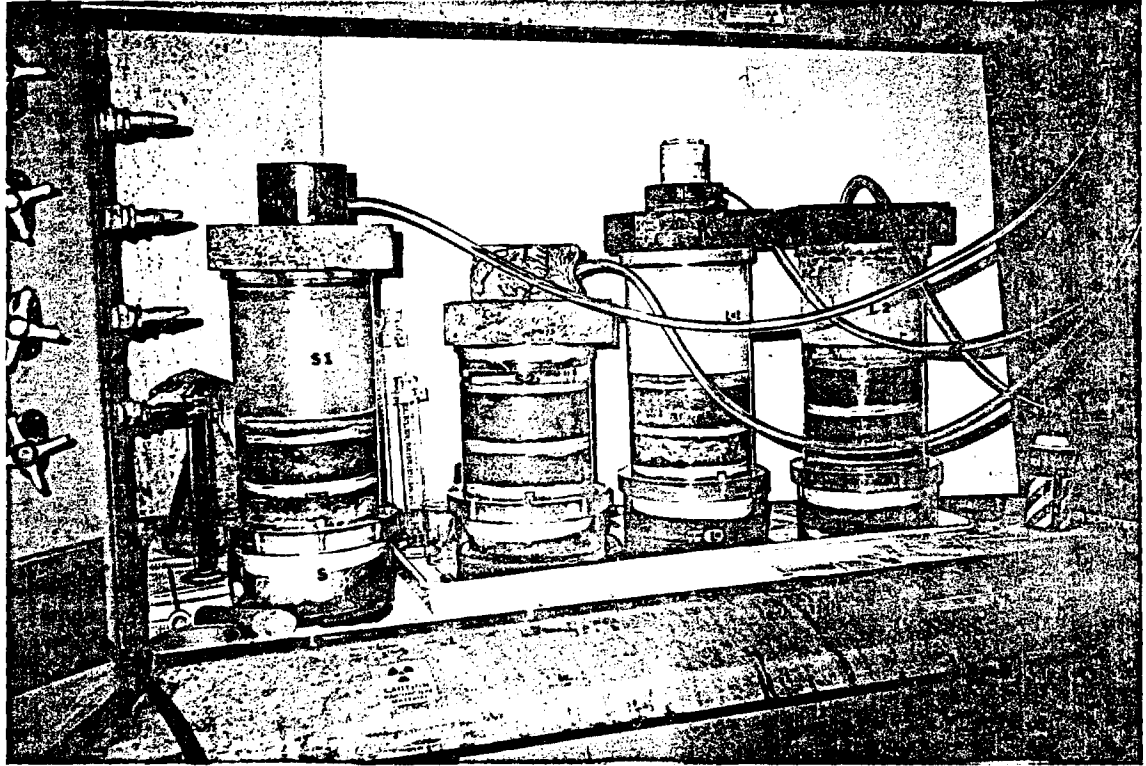


Fig. 4. Tritium diffusion tests on 2 pairs of concrete samples
(S and L, #8 and #67 stone).

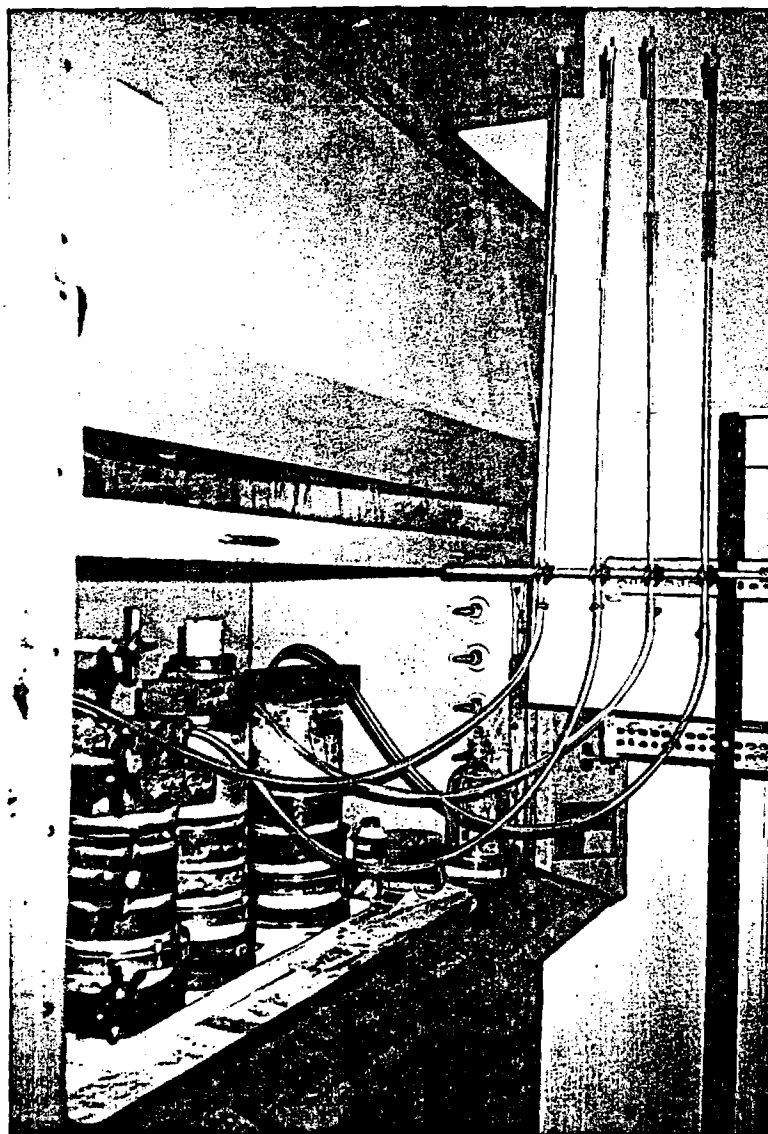


Fig. 5. View of pressurizing system.

To get uniform distribution of the tritium concentration in the effluent water (in a crystallizing dish), a magnetic stirrer was applied at the time of sampling. An Eppendorf pipette was used to get reproducible sampling, with disposable sampling pipets.

As mentioned before, a pressurized system with either air or water was used to apply hydrostatic pressure, simulating conditions in a disposal vault. The applied pressure was checked regularly by a mercury manometer. At preset time periods, sampling was done to check any increase in tritium concentration in the water in the effluent collector.

Pressures applied ranged from zero pressure to 2 inch Hg pressure (69 cm water height) and 4" Hg (138 cm water height) for 2", 3.5" and 8" tall concrete samples.

Tritium Detection

Although in the end most of the tritium counting was done by counting the water seeping through the column, initial plans assumed much slower flow rates and tritium migration by diffusion and exchange inside concrete (cement) grains. This entailed the drilling out of test cores and counting interstitial water as well as tritium in the surface layer of pulverized cement samples.

While the counting of liquid aqueous samples by conventional liquid scintillation counting is relatively straight-forward, counting powder samples is not because of settling of particles during counting and optical quenching effects. To overcome this problem, several commercial scintillation gels were evaluated with regard to their ability to maintain a homogeneous dispersion, their counting efficiency, their cost, and reproducibility.

Three commercial scintillators were tested:

Solvent-Free (made by Isolab Inc.)

Insta-Gel (Packard Instrument Co.)

Opti-Fluor (Packard Instrument Co.)

Because of the small scale of these tests and their limited duration, biodegradability of the scintillators was not considered to be a decisive factor.

The counting efficiencies of Solvent Free and Insta-Gel scintillators were compared to find the best gel-type cocktail for H-3 counting. Results showed an inherent counting efficiency of 21% for a 3:1 mixture of Insta-Gel (75% scintillator + 25% water) against a counting efficiency of only 8% for the same proportion of Solvent Free and water. The counting efficiency for Opti-Fluor, on the other hand, was 23 per cent. The results above were obtained for scintillation cocktails without adding concrete powder (Fig. 6). Fig. 6 shows the variation in counting efficiency over a range of water content.

a. Quenching versus amount of material added to scintillator.

Results presented in Table 1 and Figure 7 show a linear relationship between the S-value (determined with the external source) and the amount of material added to the cocktail (Insta-Gel).

b. Comparison between Insta-Gel and Opti-Fluor

Procedure: The same amount of powder was added to both cocktails. A higher counting efficiency was obtained with the Opti-Fluor even though the concrete powder settled down in the counting vial. The suspended concrete particles in the Insta-Gel vial resulted in a high degree of quenching due to the turbidity of the mixture.

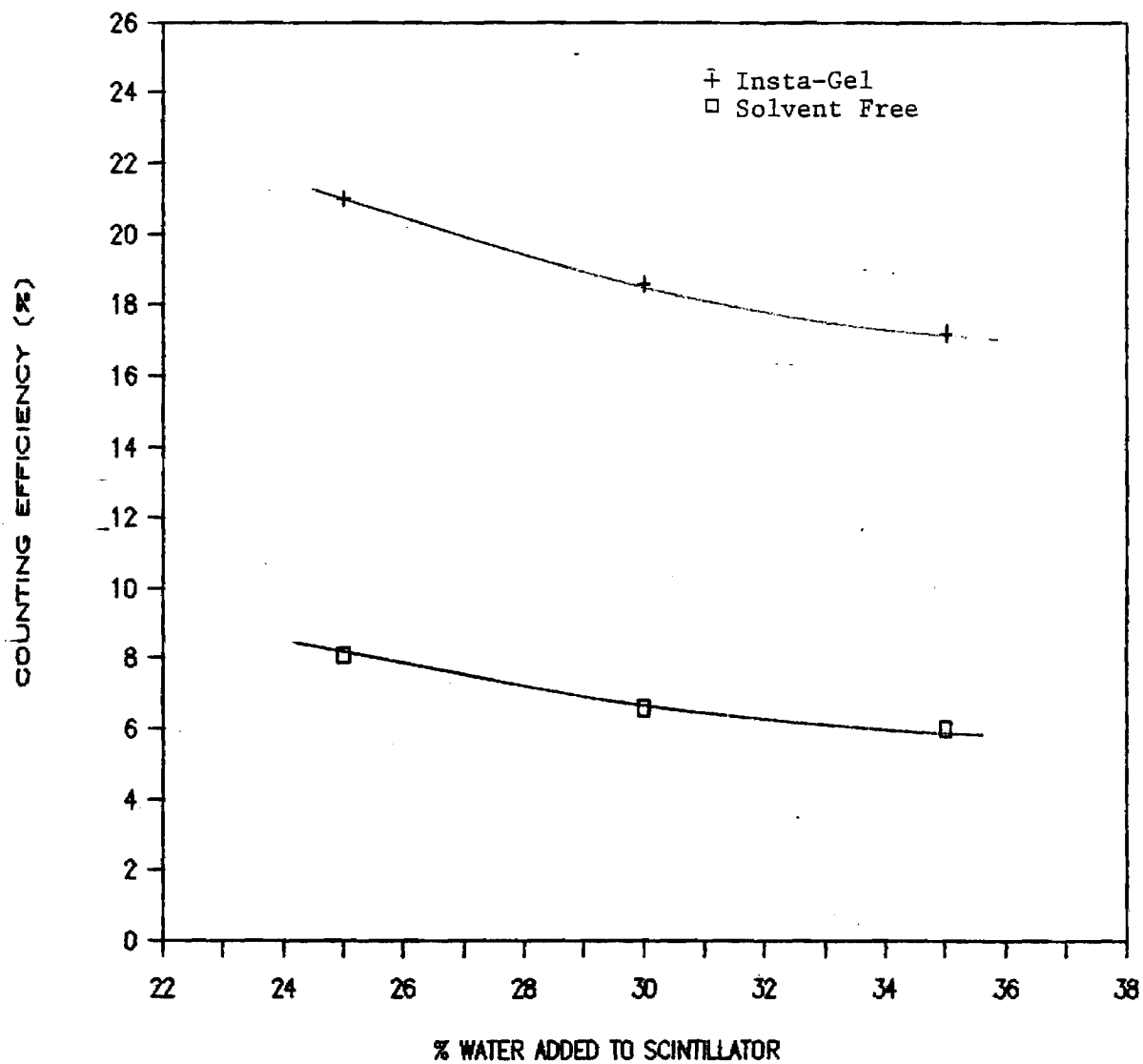


Fig. 6. Counting efficiency dependence on the amount of water added to scintillator to form gel.

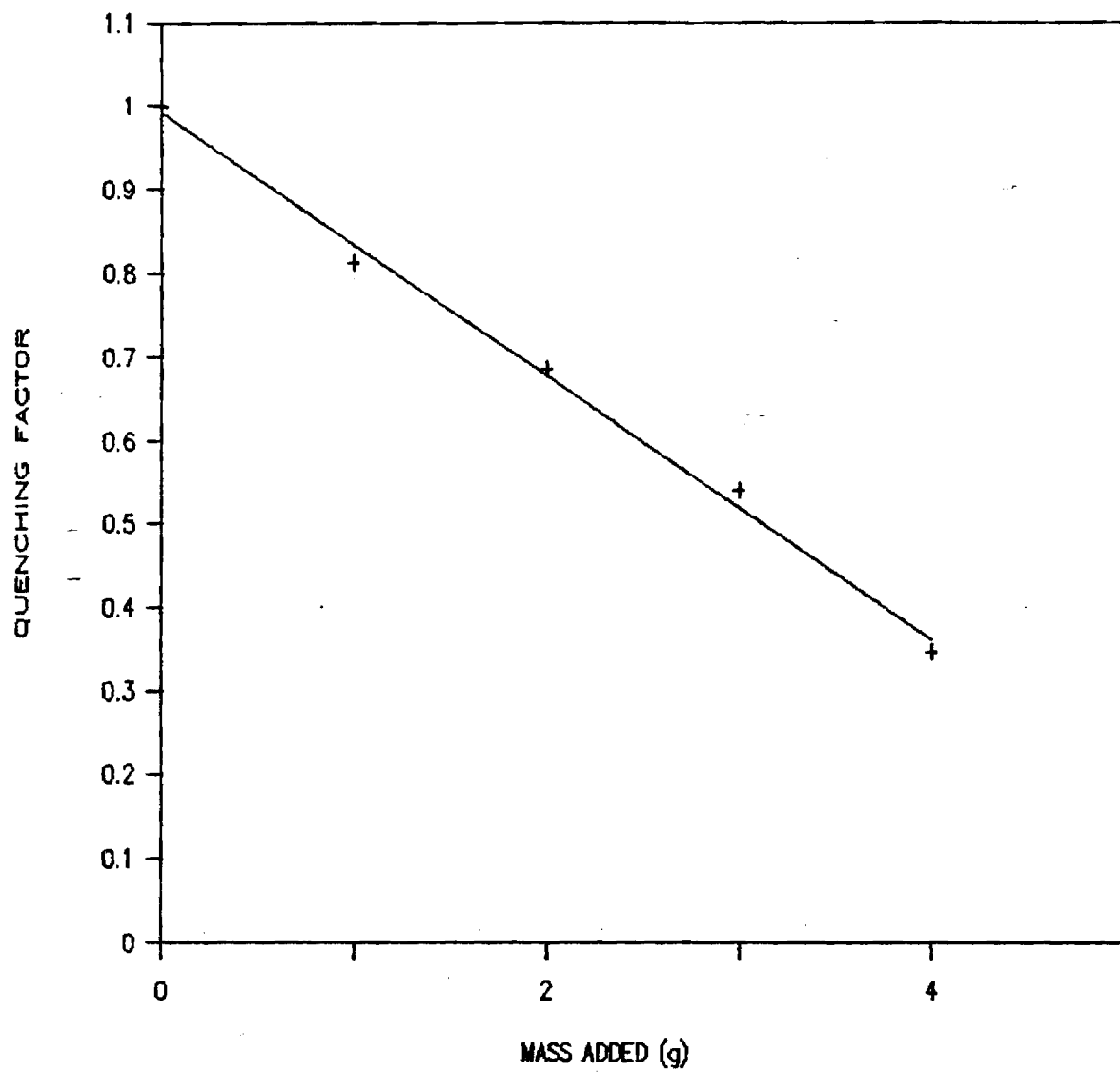


Fig. 7. Quench curve for concrete powder in Insta-Gel.

Based on the results above we selected the Opti-Fluor cocktail for all measurements.

c. Choice of sampling method (powder versus chips)

Procedure: Tritium was poured on the top of some short concrete columns; the bottom of the concrete columns was kept in water; upon arrival of H-3 at the bottom of the column (confirmed by water sampling), break the column to get chips and powder; add a certain amount of chips or powder to scintillation cocktail and count.

Result: A higher counting yield was observed for samples of the chip type when compared to the powder type. The ratio between chip-type and powder-type samples was found to be around 1.4.

We noticed that for both types of samples, the count rate increases as a function of the time elapsed after sampling, reaching an equilibrium value in about 7 days. For the powder samples, the ratio of the equilibrium to the initial value was found to be of 1.30 (See Fig. 8). For the chips, this ratio was equal to 1.7 (Fig. 8). This may be related to surface area, due to surface tritium migration into the scintillation solution.

Due to the type of concrete blocks that would be used in the next stage of the experiment (large columns), it was decided to use powder samples to determine the H-3 profile inside the concrete layers.

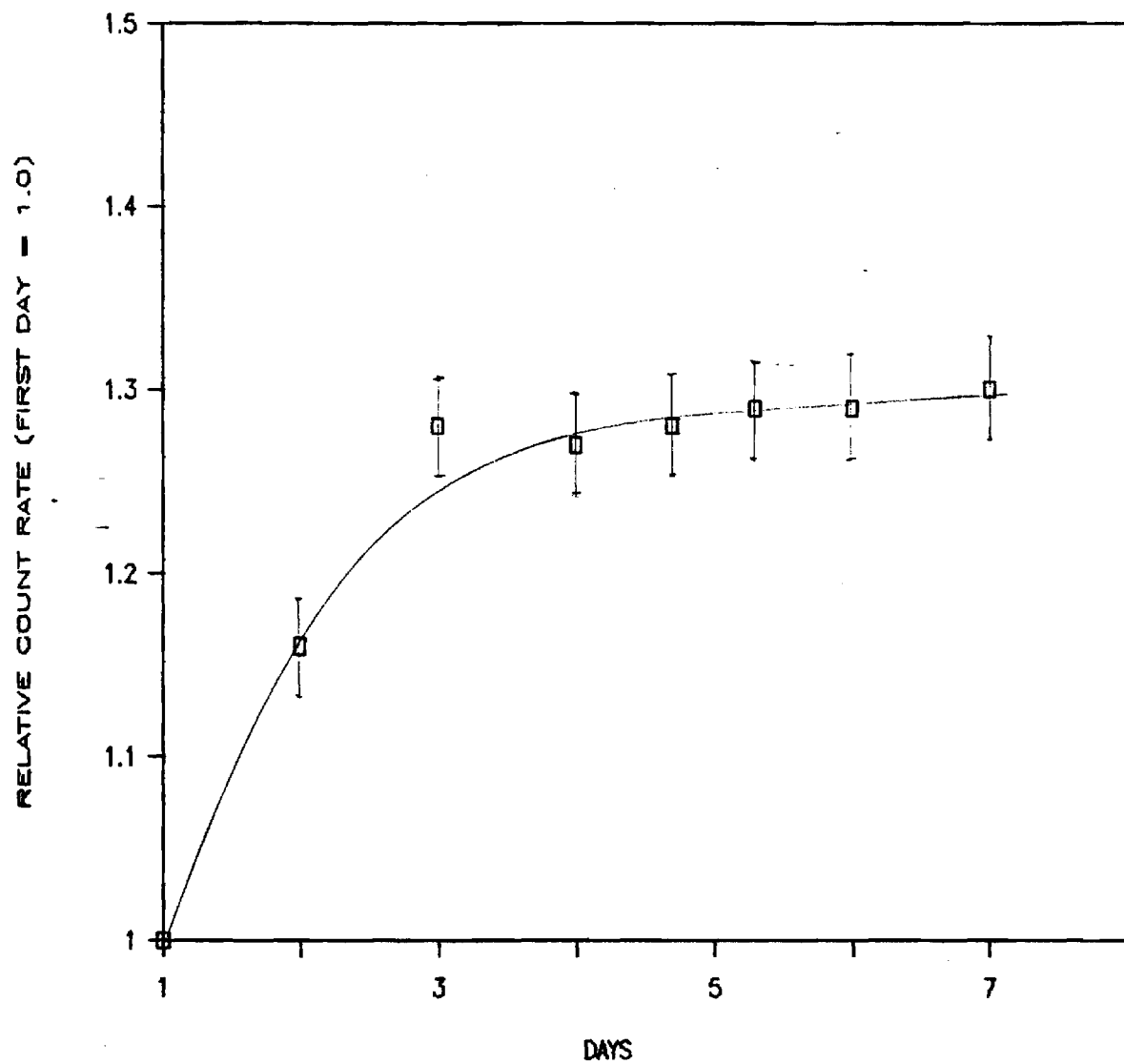


Fig. 8. Diffusion of H-3 out of concrete particles (powdered samples) (Normalized to 1st day)

TABLE 1

QUENCHING FACTOR AS A FUNCTION OF THE AMOUNT
OF SOLID ADDED TO THE COCKTAIL

<u>SAMPLE #</u>	<u>SCINTIL.</u> (ml)	<u>WATER</u> (ml)	<u>CONCRETE</u> (g)	<u>S-VALUE</u>	<u>Q. FACTOR</u>
24	12	4	control	0.623	2.0
25	12	4	1	0.506	0.812
26	12	4	2	0.426	0.684
27	12	4	3	0.337	0.541
28	12	4	4	0.234	0.376

* Surewall; Particle size: -30 to +60 mesh;

** S-values represent the average of 3 counts;

*** Factor = Quenching factor, normalized to S = 0.623

Method of Analysis

In order to estimate infiltration velocity (initial transient), infiltration rate (steady state), and diffusion coefficient, which are important factors to describe tritiated water behavior inside the concrete sample, several types of sample were prepared at the concrete laboratory at Georgia Tech. Those samples were composed of rectangular samples 1" x 1" x 3", 1" x 1" x 2", 1" x 1" x 4", 2" x 2" x 4", 3" x 3" x 4" in size and cylindrical samples, 6" dia x 2", 6" dia x 35" 6" dia x 8" for the standard formulation as well as 6" x 8" cylinders with the smaller size of stone (#8).

In the analysis of rectangular samples, two methods were used to calculate transient infiltration velocity and diffusion coefficient. Because flow conditions in a porous medium generally follows a Gaussian distribution, this distribution was assumed to be suitable in the analysis of the behavior of tritiated water.

The first method was to take out chip samples from inside the concrete by use of a chisel and hammer several time periods after setting up the system. Those samples were counted in the Liquid Scintillation Counter in the Old Civil Engineering Building, Environmental Lab.

The second method was to sample and count the water at the bottom of the columns. The columns were left for the designated time period without any destruction. By checking the increase of tritium concentration as a function of time, the transient infiltration velocity could be calculated.

The following equations were used in calculating the transient infiltration velocity and diffusion coefficient:

$$C(x, t) = C_m \exp \left\{ - \frac{(x - x_m)^2}{4Dt} \right\}$$

$$\alpha = \int_{k_\alpha}^{\infty} \frac{1}{\sqrt{2\pi}} e^{-\frac{x^2}{2}} dx$$

where $C_{(xt)}$ = Concentration at position x and time t .
 C_m = the max. concentration
 x = distance from the peak position
 D = diffusion Coefficient
 t = time
 α = Area under the normal distribution from k_α to ∞
 k_α = the coefficient in normal distribution

$$\alpha = 0.5 \text{ at } k_\alpha = 0$$

$$\alpha = 0.001 \text{ at } k_\alpha = 3$$

In the first method, three data points were taken to calculate the peak position, the max concentration, and the diffusion coefficient at a given time. By comparison of those three values at several time periods, transient infiltration velocity was determined.

The other approach was used in the second method. Just by checking the increase in tritium concentration in water without any destruction of the rectangular samples, the transient infiltration velocity could be estimated. It was assumed that the increase of tritium concentration was directly related to the movement of the peak position in the moisture profile located at the maximum concentration as the active pulse moved downwards.

The values obtained by both methods showed good agreement with each other. Those values are shown in Table 2.

The 6" cylinders were sawed up to provide slices of different thicknesses. For those samples a different method was used. Before the experiment, the concrete samples were soaked for a long time (~1 month) in a water bath to get saturated. It was assumed that a minimum detectable 0.1% increase of tritium concentration per unit volume in water at the bottom, compared to the initial tritiated water concentration would result from the movement of tritiated water to reach the bottom. Under this assumption, the net increase in the tritiated water concentration was checked as a function of time from the beginning of the experiment. The time required to exceed a 0.1% increase in activity was related to the sample thickness to get the transient velocity.

In order to allow an estimation of migration rate (steady-state infiltration velocity), net increases of tritium concentration in water were checked with time. After a linear rise in tritium concentration was reached, the slope was determined by a linear regression method. The slope obtained permitted calculation of the steady-state migration

Table 2
Results of Wetting Tests

Type	Sample Size (in.)	Test method	Measured wetting rate (cm/day)
Rectangular	1x1x3	LSC, chip samples	3.1 @ 1 day, 1.7 @ 3d.
	1x1x2	init. dry, chip	not detectable
	1x1x4	LSC, powder samples	0.75 - 6.7
	2x2x4	" 0.55 - 7.6	
	3x3x4	"	1.5 - 6.9
Cylindrical	6x2	atm. pressure, finished	0.9±0.2
	6x2	atm. pressure, unfinished	40.6±2.8
	6x2	50 torr excess, finished	1.3±0.2
	6x2	100 torr excess, finished	4.0±0.7
	6x8	atm. pressure	10.2±0.7 (int. crack ?)
		50 torr excess	13.5±1.4 "
	6x3.5	100 torr excess	2.4±0.2
	6x8 (No. 67)	100 torr excess	4.5±0.5
	6x8 (No. 8)	100 torr excess	nil after 15 days

velocity (or rate). The adjusted slopes from various samples were divided by the cross-sectional area of the sample for a given porosity of samples. Migration velocity (steady-state) can be determined by dividing the migration rate by the sample porosity.

EXPERIMENTAL RESULTS

1. Water absorption

Initially, dry concrete samples were considered as the test samples to provide the basic information for the remaining experiments. For that purpose six rectangular samples (1"x1"x2") were prepared and exposed for a limited time to wetting from the top surface. It was found that no significant and detectable infiltration of tritiated water took place, because of the complete absorption and retention of tracer water in the top layer of the concrete samples. It was concluded that fully dry concrete samples were not representative of practical conditions and did not simulate the disposal vault material. In order to verify this condition, water absorption tests of concrete were done as an initial stage of this project. In this test, 1.5" and 6.2" thick concrete samples, 6" in diameter, were held in a stand just touching a water surface. The change of weight of concrete was checked and recorded as a function of the time. It was found that it didn't take very long to reach saturation in both samples though differing in thickness. The results of the water absorption test are shown in Fig. 9. On that basis it was decided to use wetted concrete samples for the main test program.

Because of the importance of determining wetting rates, transient migration velocity, steady-state migration velocity and diffusion coefficient were obtained for different size samples.

Seven rectangular water-saturated samples, obtained by the ASTM C20-83 method, were checked to determine infiltration rates for instantaneous tracer injection. The rate of wetting the samples was almost the same as that described in other references. Moreover, the reduction of that rate was found to decrease with time, as described in the same references. It is generally known that the progress of hydration and the tortuosity effect of stone would reduce the wetting velocity. In addition, porosity in concrete is known to vary with the water content used in concrete fabrication. When a high fraction of water is used, the sample becomes more porous. Such porous samples will give rise to a higher rate of wetting. For

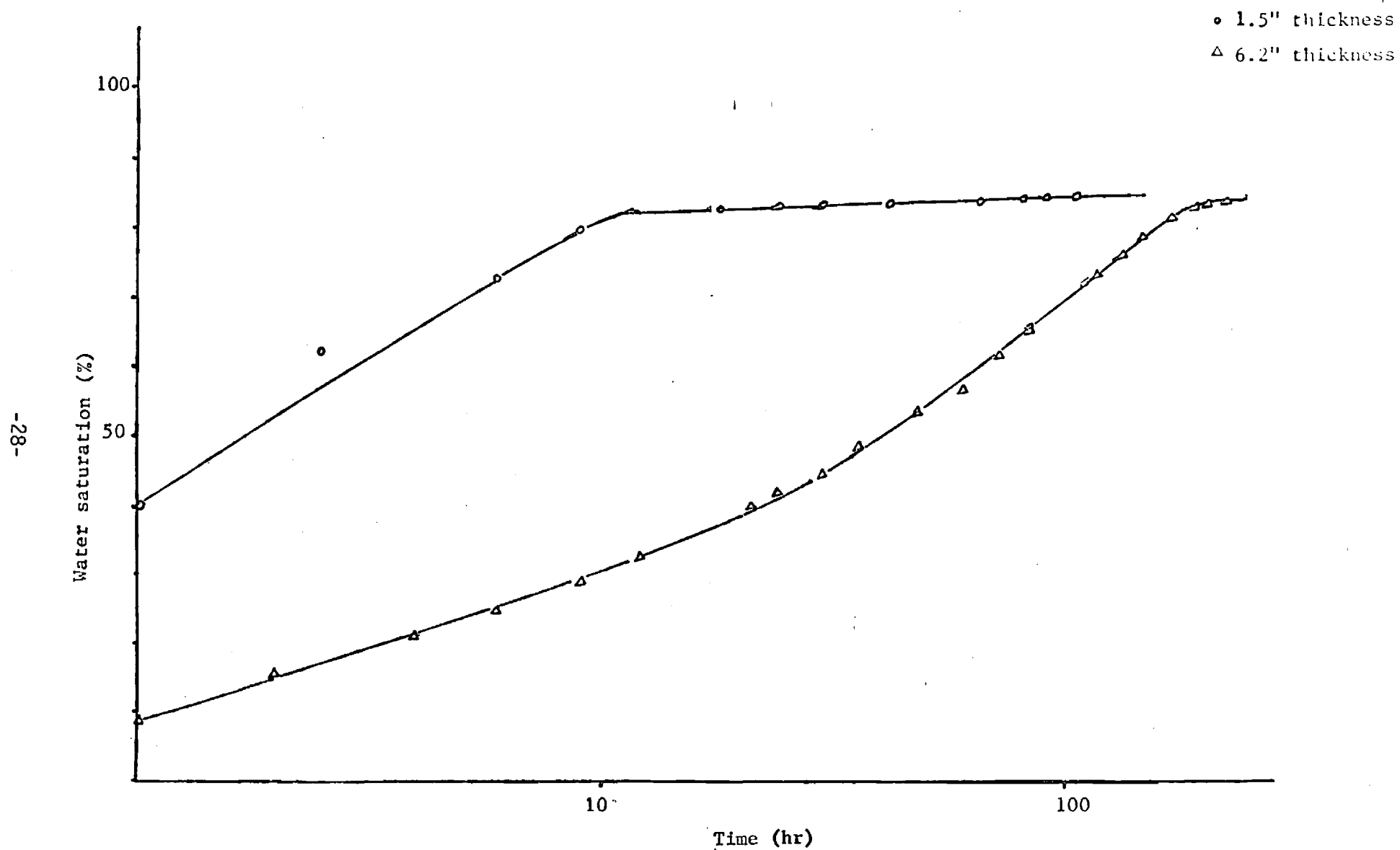


Fig. 9. Water absorption tests.

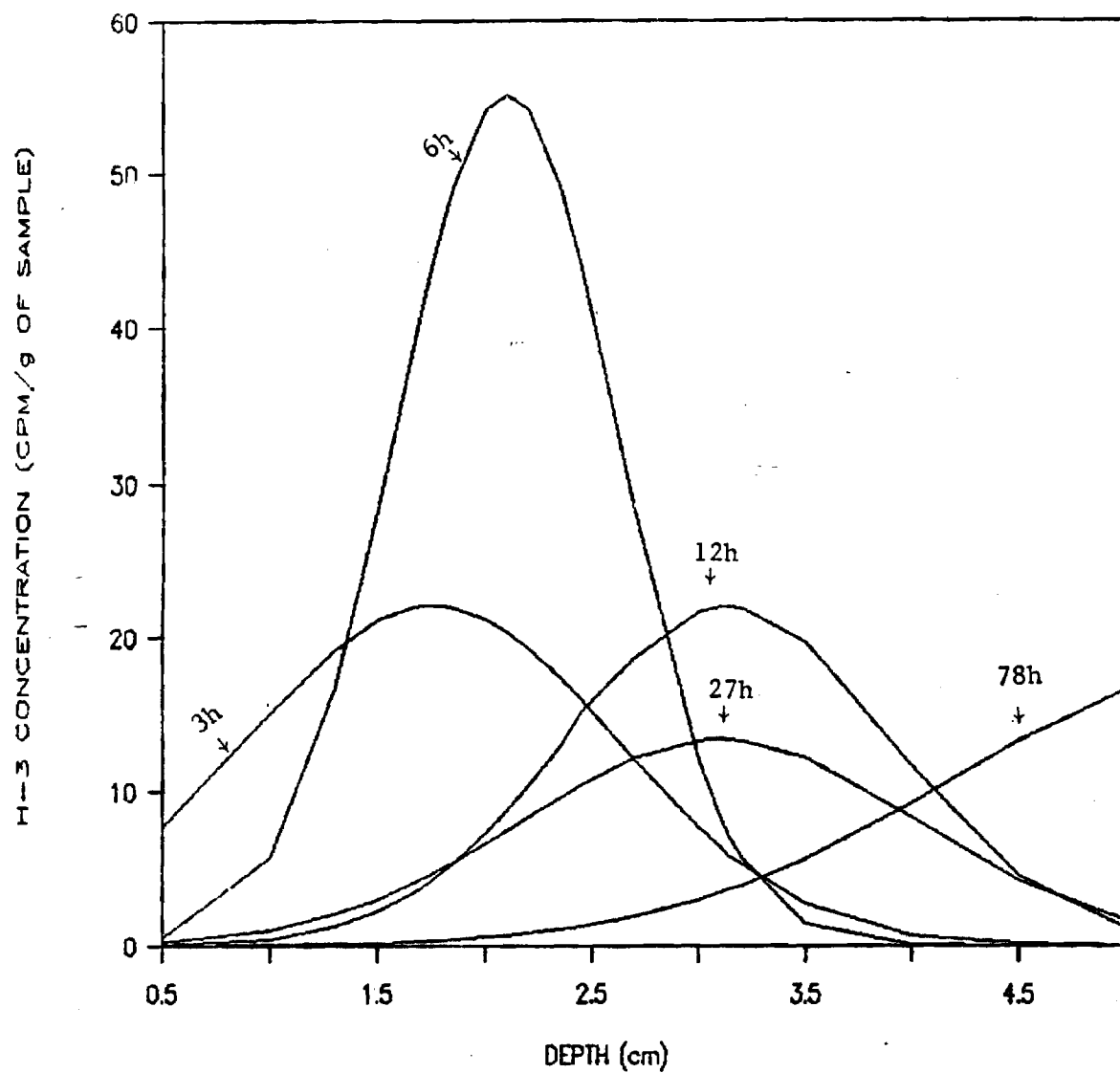


Fig. 10. H-3 concentration profile for wet rectangular samples (1"x7"x3")

this reason attempts were made to obtain uniform porosity by controlling the water content in the concrete mixture. Numerous samples were fabricated at the same time to avoid variations in porosity between samples used in different experiments.

2. Migration Tests: short columns

After basic parameters had been measured, the dependence of migration rate on sample size, composition, surface finish, applied pressure, and sample thickness was determined.

In order to determine the effect of sample size, 1"x1"x4", 2"x2"x4" and 3"x3"x3" sized samples were prepared and treated in the same way as before, with the same tracer concentration. Deionized water was placed in contact with the bottom end of each concrete test sample until some meaningful increase of radioactivity above the background level was observed. The samples were taken out and left for 3 days in a refrigerator to freeze. Freezing was the most effective method to avoid any water loss when drilling inside the test sample.

It was found, as expected, that the larger samples resulted in higher migration with better counting statistics and less variation due to surface porosity effects. Fig. 10 shows the activity profiles observed for a wet rectangular column, by drilled powder samples, as a function of time. The smoothed profiles are matched to Gaussian curves with substantial errors, as shown by the variations in the areas under the curves. Yet the relatively rapid movement of the tracer pulse is evident.

In order to determine infiltration rate in a slab of concrete, a 6" diameter 2" high concrete slab was used for experiments. Initial tests made use of deionized water and results were analyzed by a gravimetric method (the water volumes taken out above the fixed water level). Towards the end, when the migration rate became very slow and hard to detect, tritiated water was detected in the effluent. It was found that the migration rate amounted to $2.8 \pm 0.3 \times 10^{-3}$ cc/cm² day under steady-state conditions. To get this steady-state result, linear regression fitting was used with an acceptable correlation value. Much higher migration were observed

with top slices and rough sections of concrete, which had higher porosity. Fig. 11 compares the permeability of rough, unfinished and smooth, finished specimens.

3. Long-column tests

As has been mentioned before, thin concrete layers are not representative of thick concrete layers. For that reason, longer columns, at least 8-inches long have been used for terminal measurements. Unfortunately, it was impossible to get larger sample than 10" thick samples in practice. In this project, 8" (20 cm) thick samples with 6" (15 cm) diameter were used to simulate the actual disposal wall conditions. In comparison with thinner samples, for the general tests of migration rates, 3.5" and 8" thick samples were mounted inside a Lucite tube with leak-tight conditions set up with plaster and absorbent paper annuli to avoid wall channeling. As expected, the thicker samples showed much lower infiltration rates and a lesser steady-state migration velocity. However, the rate of wetting, i.e. the velocity of any wetting front, did not show any difference between thin and thick samples.

Once steady state conditions were obtained, about 15 days after the start-up of the experiment, the internal tritium profile in the concrete sample was checked by drilling, sampling, and counting in a liquid scintillation counter, in the form of powder samples. It was found that the diffusion coefficient in the thick sample was almost the same as for thin samples, of the order of 10^{-5} cm²/sec. Using this diffusion coefficient the migration rate was calculated with Fick's equation. As a result, it was found that the agreement between the calculated value and the experimental one was good, within one order of magnitude. There were some variations in internal tritium concentrations due to the existence of some preferential flow pathways resulting from the random distribution of stone and some boundary leakage.

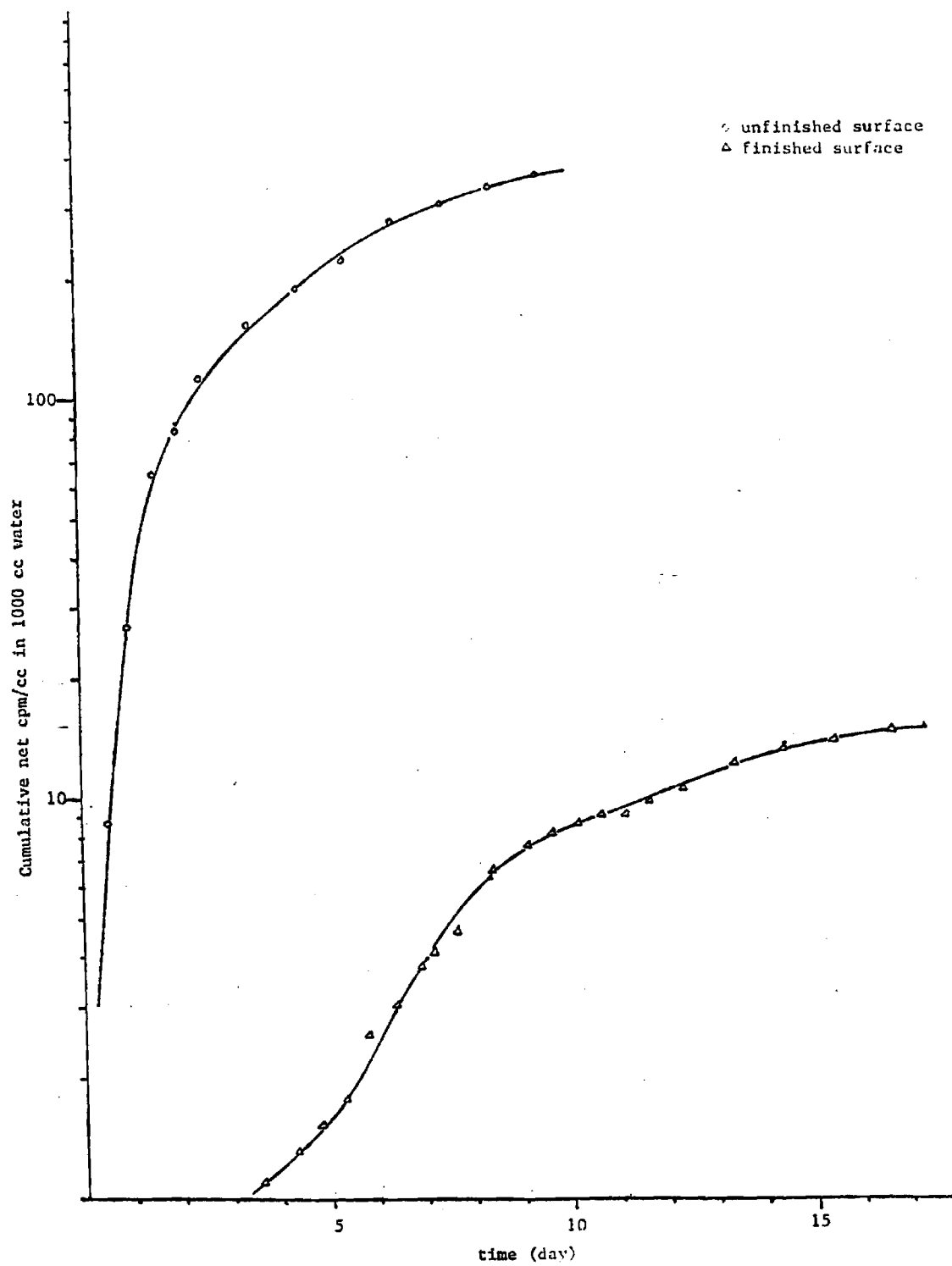


Fig. 11. Migration test for unfinished surface and finished one under no pressure.

4. Effect of stone size

The recommended concrete formulation used No. 67 stone, but because of the observed high migration rate, it was decided to check if a smaller aggregate size would be helpful.

Smaller size stone, No. 8 (3/8" - No. 8 sieve size), was used to test for any stone-size effect, instead of the No. 67 (3/4" - No. 4) stone recommended for the storage vault. It has long been known that stone itself is less porous and permeable than the other porous concrete components. During the comparison of stone size effects one, it was found that the No. 8 stone size sample was relatively less permeable than No. 67 stone sample, as shown in Fig. 12. It is probable that the existence of the larger stone interface area was responsible for this lower permeability. For the same weight of stone added in the concrete sample as No. 8 size stone, the interface area was as large as with No. 67 stone. In addition, the tortuosity effect due to the higher number of particles of stone is believed to cause a lower permeability in rate for the No. 8 stone sample.

5. Effect of column length

A series of migration tests were performed by measuring the tritium content in the effluent container, by liquid scintillation counting, for columns of various length, as illustrated in Figs 3 and 4. The results of these tests are presented in Fig. 13 for columns 2, 3.5 and 8 inches (5, 8.75 and 20 cm) in length. It is clear that migration for the longer columns approaches the steady state migration. Using the slope of those curves, an asymptotic value for the migration rate of about 8×10^{-4} ml/cm²-day is calculated, as shown in Fig. 14. It seems evident that measurements at greater thicknesses would not result in any significant change in permeability.

A more significant factor, which is hard to qualify, is the degree of "finish" of the sample. Well compacted, deaerated concrete has a lower porosity and hence a lower permeability. This is shown strikingly in Fig. 11, which compares the effluent activity with time for a "finished" and an "unfinished" column. The difference is of the order of 30-fold.

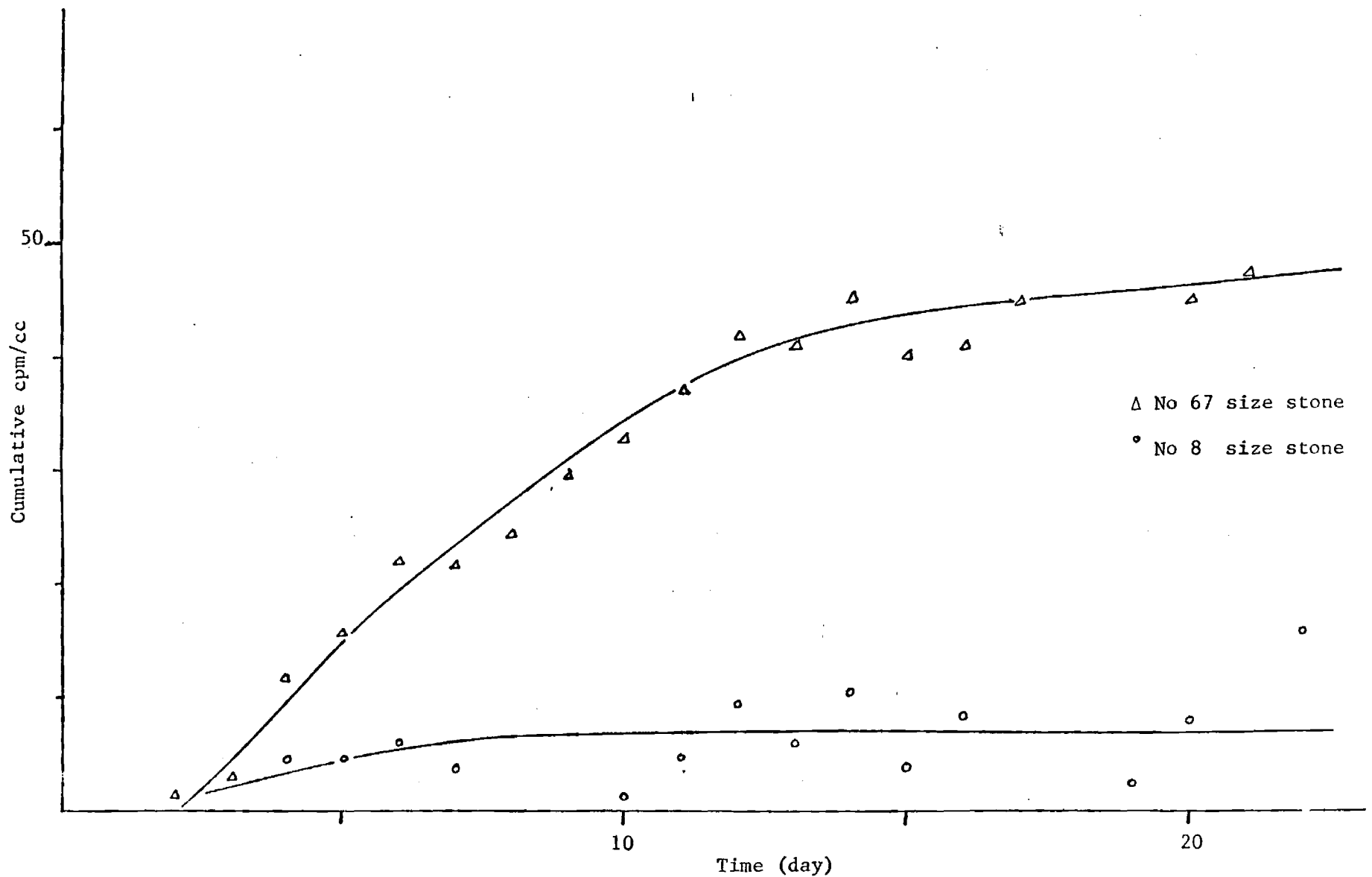


Fig. 12. Comparison of No. 67 and No. 8 columns.

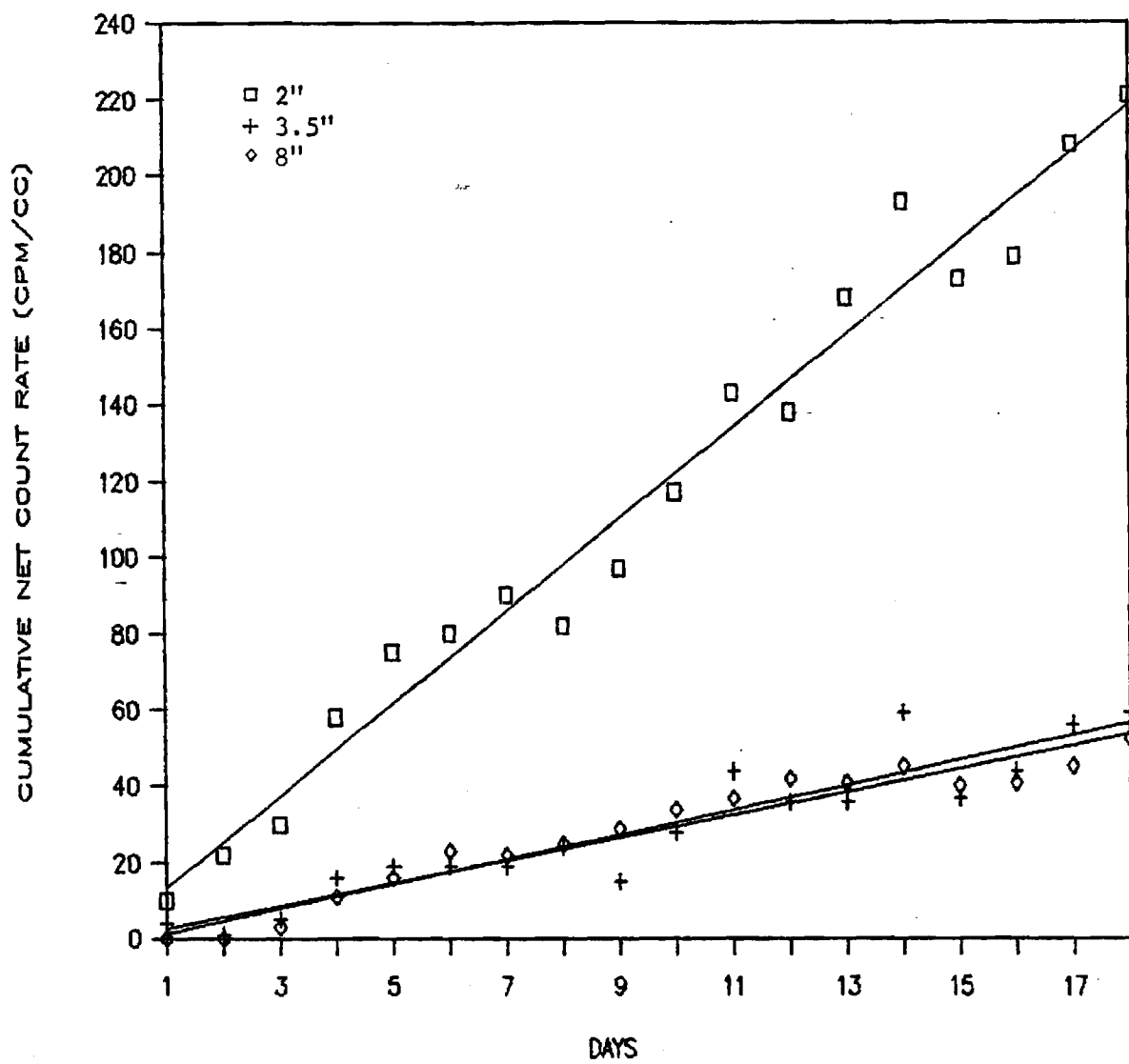


Fig. 13. Cumulative increase in tritiated water concentration as a function of time, for different concrete slab thicknesses

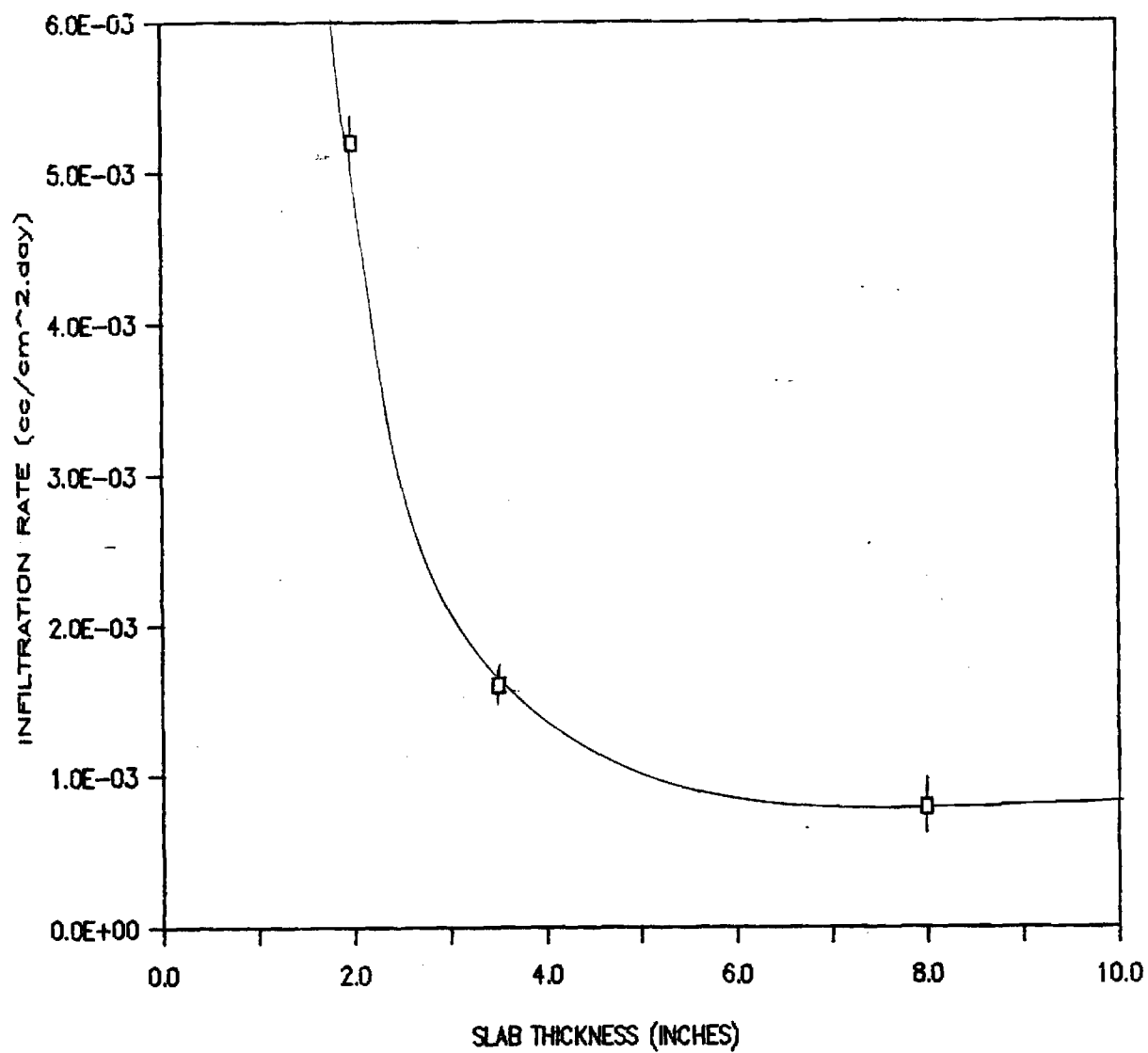


Fig. 14. Change in infiltration through concrete slab as a function of slab thickness.

6. Effect of pressure

For any poorly permeable medium, migration (or hydraulic conductivity) is a function of applied pressure for thin layers, whereas for thick layers the hydraulic conductivity itself give rise to a terminal migration rate. A series of tests were performed under airborne pressure using a mercury manometer and a series of tests using a water column of 60 or 120 cm of water (810 or 860 torr), both of them shown in Figs. 4 and 5. Fig. 15 shows the results obtained for migration as a function of time for 2-inch columns for three different pressures. The flow rate increases significantly for the higher air pressure, resulting in a doubling in infiltration rate at the higher excess pressure (Fig. 16).

For the longer columns, 8" (20 cm) long, the flow rate observed was somewhat lower at the higher pressure, though the slope was the same (Fig. 17, 18). This result was unexpected and a separate test, comparing duplicates of both concrete samples were run to verify the result. The results in Fig. 18 may indicate the presence of small cracks in the sample. Fig. 19 displays the profile of the average-tritium concentration as the function of depth under 50 cm of water pressure. It is evident, that a steady concentration at depth was obtained.

DISCUSSION

In the last section, we discussed all data obtained so far. In order to avoid and/or reduce any significant migration of tritiated water out of the disposal vault, several factors must be considered; surface porosity surface finishing and defects in the concrete may be among them. Because the surface porosity is largely affected by the water content in the composition of concrete, it is critical to reduce the content of water as low as possible, even though there are some practical and structural considerations determining the minimum water content. As another consideration, the smoothness of the surface is very important; a smoothly finished surface is able to reduce the infiltration rate significantly. It is believed that the absorption of water from the surface can be reduced by deaerating and smoothing the concrete surface.

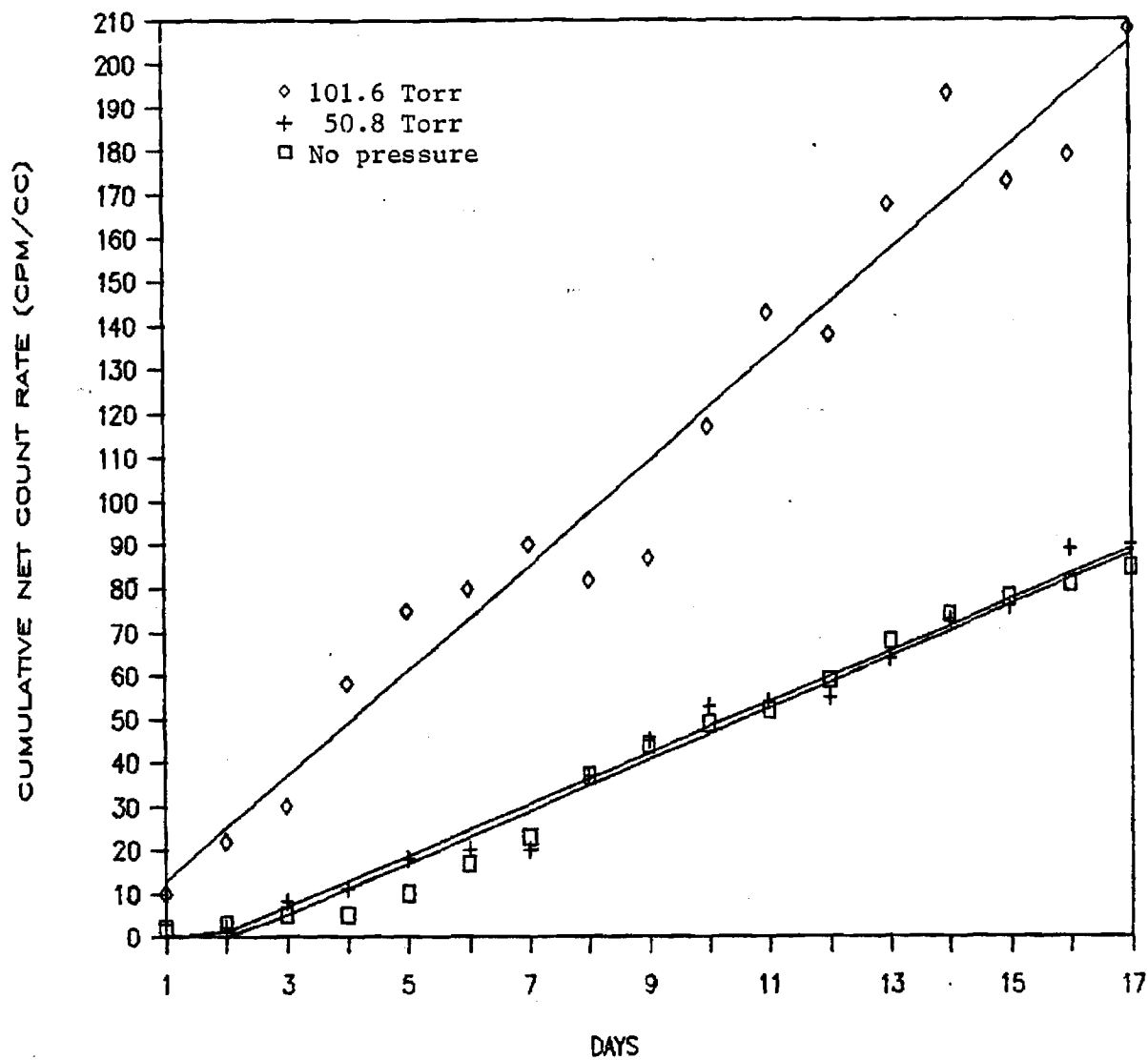


Fig. 15. Effect of applied pressure on tritiated water infiltration rate (2" thick sample).

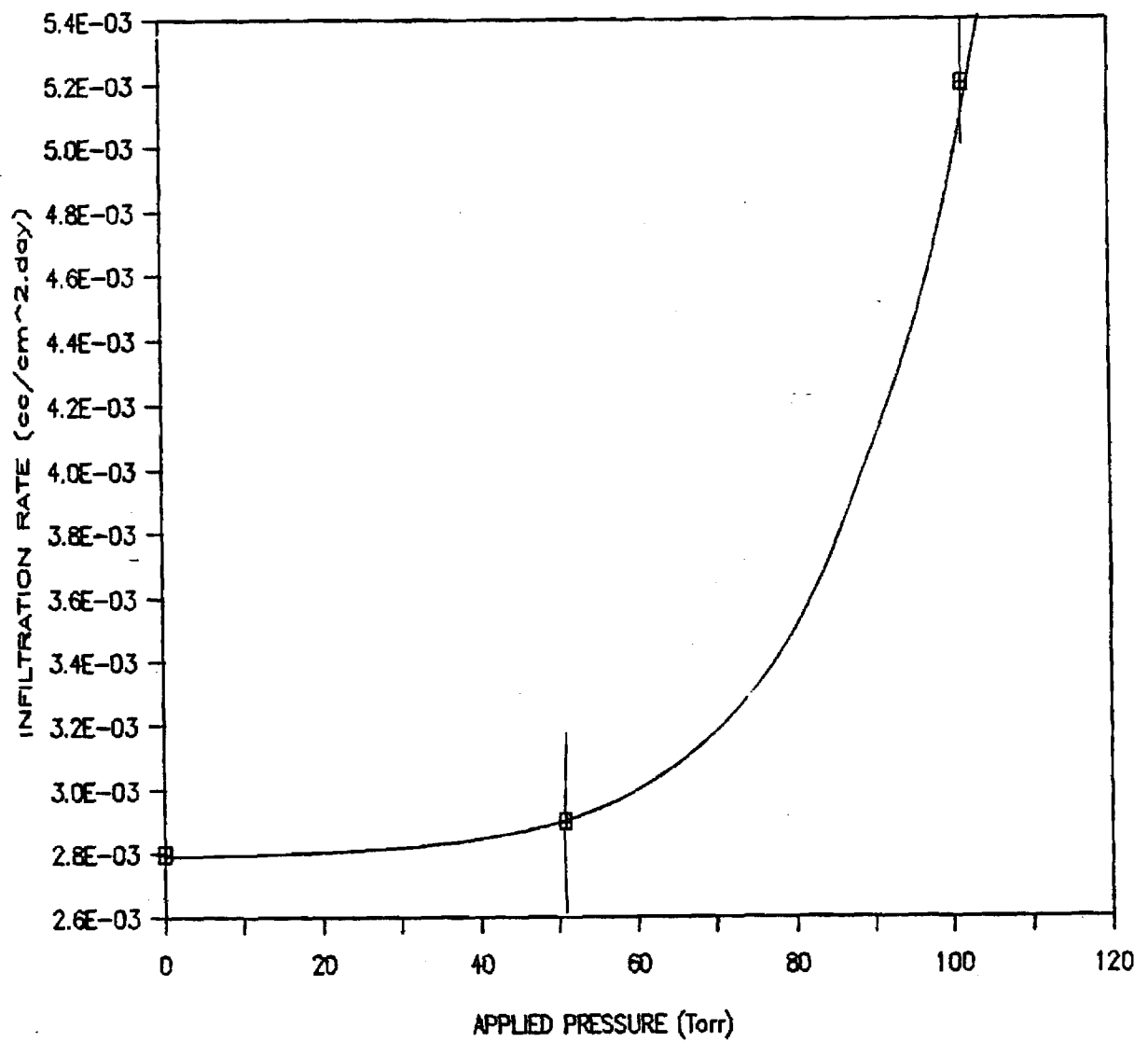


Fig. 16. The effect of applied pressure on infiltration through 2 inches thick slab

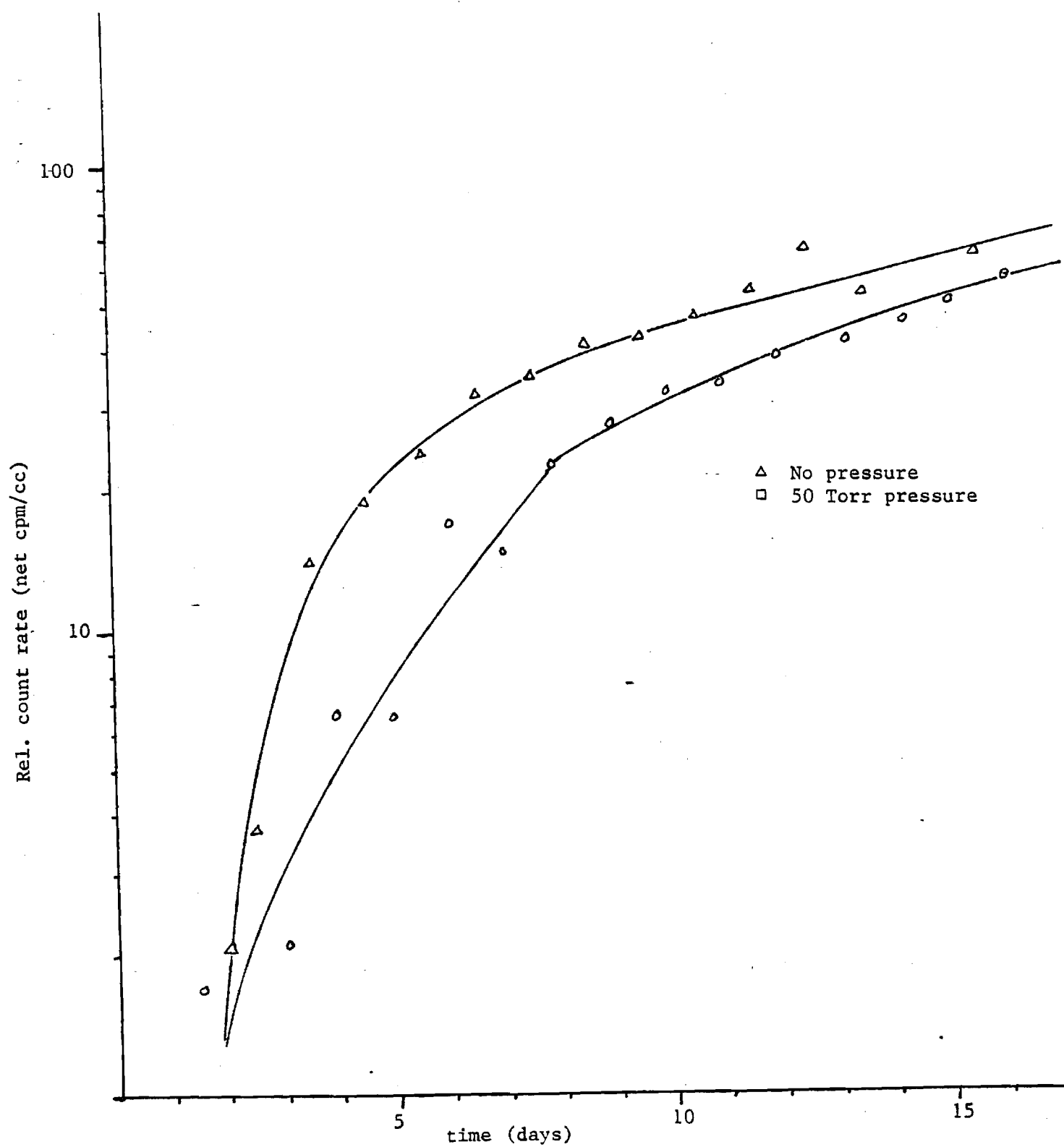


Fig. 17. Comparison of infiltration with different pressures for 8 inch thick samples.

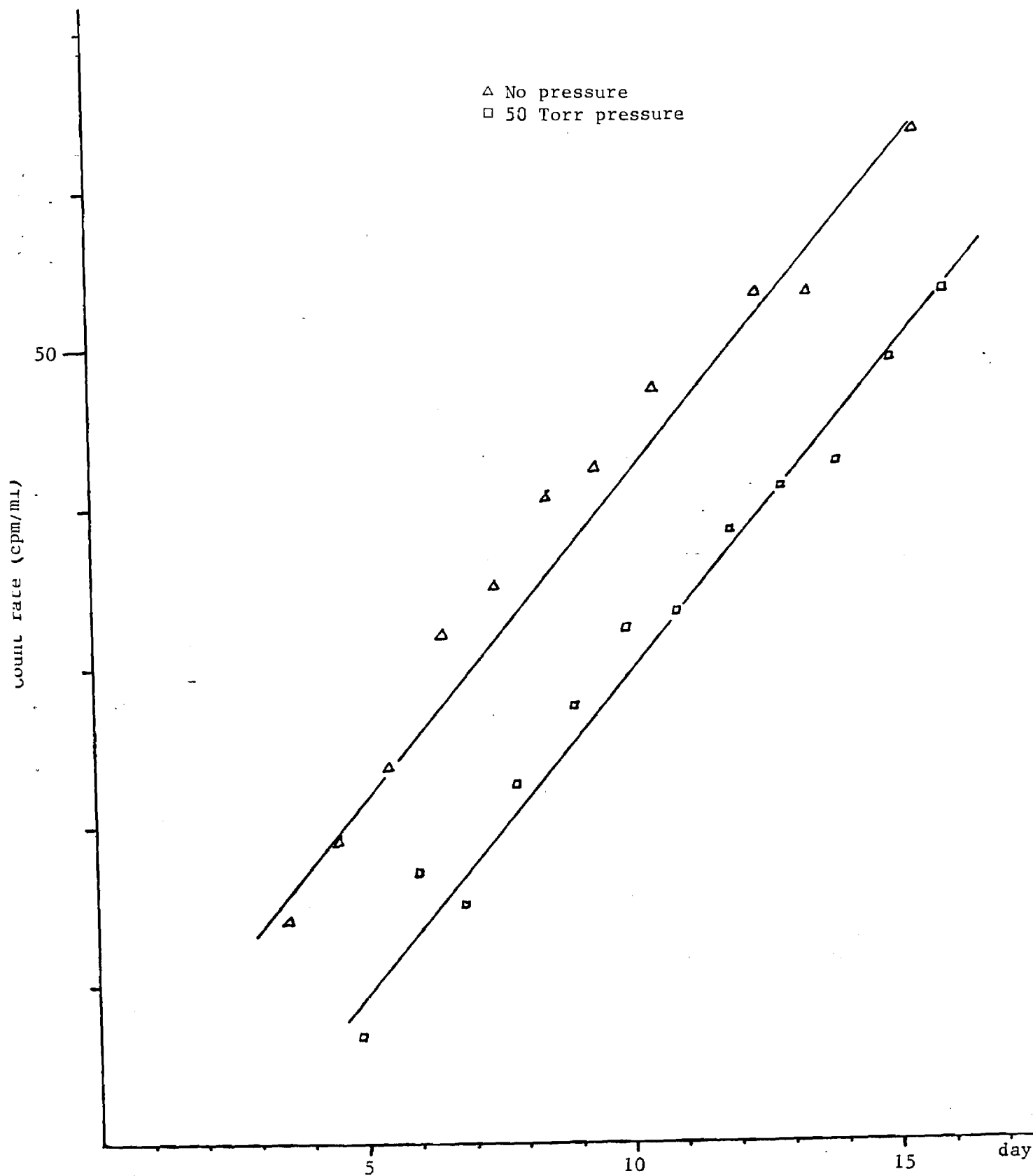


Fig. 18. Comparison of migration time with different pressures for 8 inches thick sample.

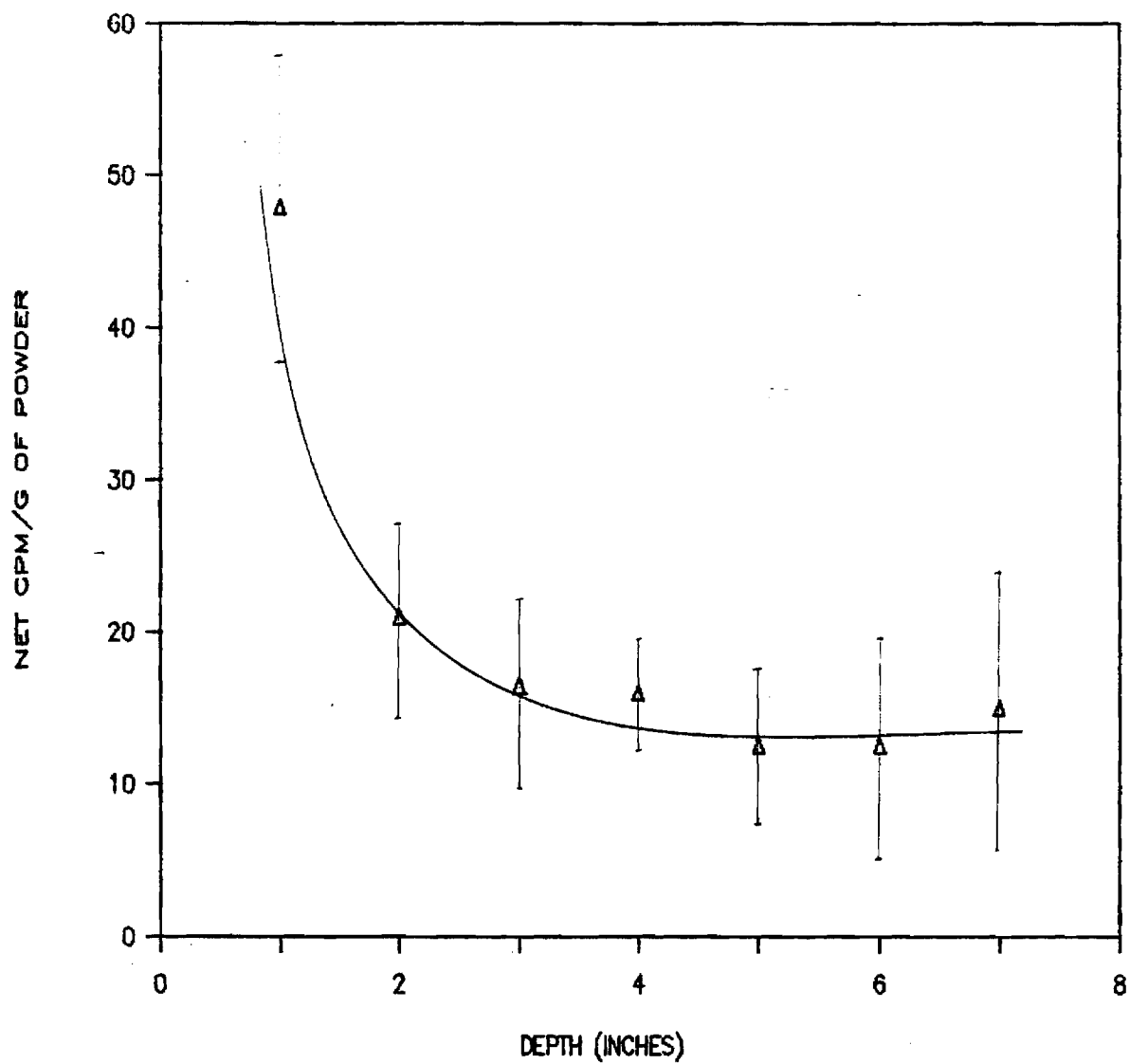


Fig. 19. Final Average profile at end of test, 8' cylinder, 810 Torr.

Cracks and defects inside the concrete would be serious and harmful. To observe this effect, defective concrete samples were made deliberately by hitting them several times with a hammer. For such a sample high infiltration rates were found in the tests.

Owing to the differences in density between stone and cement, concrete non-uniformity gives rise to other problems in actual systems. It was found that a higher number density of stone existed at the bottom of the concrete than at the top. It was noticed in the experiments that the migration rate of the bottom layer was much less than that of the top one. This would be very hard to control at an actual storage tank, and calls for careful mixing as a low-water content slurry.

As mentioned above, both steady-state, i.e., continuous tracer input and pulse input were used to add the tracer onto the top of the concrete sample. The pulse input method was used to obtain some basic data for the later experiments with the rectangular samples. On the basis of those results, continuous steady-state tracer input, in which the tracer is kept in touch with the top surface of the concrete sample, was used to determine the rate of wetting, steady state migration and the diffusion coefficient. No significant difference in output data seems to result from the two methods of tracer injection.

In applying air and/or water pressure to the experimental system, 4 inch mercury pressure, which was equivalent to about 100 torr, was the highest level that could be obtained in our system. In order to allow higher pressure in our system a more effective leak tight system and/or pressure device would have to be constructed. However, there was no indication that tests at higher hydrostatic pressures would have significantly altered the main conclusions.

The two samples that had been prepared by vibratory compaction resulted in significantly lower migration rates, as shown in Fig. 20. The use of No. 8 stone reduced effluent activity to negligible levels over the 70-day period of the test while the No. 67 material showed a finite improvement over previous tests.

Table 3
Summary of Migration Test

Type	Sample Size (in.)	Pressure	Migration rate (cm/day)	Diffusion coeff. (cm ² /sec)
Rectangular	1x1x4	atm.	$2.5 \pm 0.1 \times 10^{-2}$	3.3×10^{-5}
	2x2x4		$4.3 \pm 0.1 \times 10^{-2}$	3.4×10^{-5}
	3x3x4		$5.0 \pm 0.1 \times 10^{-2}$	1.1×10^{-4}
Cylindrical	6x2 rough	atm.	$1.39 \pm 0.05 \times 10^{-1}$	
	6x2 finished	atm.	1.4×10^{-2} (5 days)	
			$2.8 \pm 0.3 \times 10^{-3}$ (45 d)	
	6x2 finished	atm. + 50 torr	$2.9 \pm 0.3 \times 10^{-3}$	
	6x2 finished	atm. + 100 torr	$5.2 \pm 0.2 \times 10^{-3}$	
	6x3.5 rough	atm. + 100 torr	$1.6 \pm 0.1 \times 10^{-3}$	
	6x8 (No.67)	atm. + 100 torr	$8.0 \pm 2 \times 10^{-4}$	
	6x8 (No.8)	atm. + 100 torr	n.d.	
	6x8 (cracked?)	atm.	$9.8 \pm 0.5 \times 10^{-3}$	
		atm. + 50 torr	$9.4 \pm 0.5 \times 10^{-3}$	
	6x8	atm. + 50 torr		$3.3 - 7.1 \times 10^{-5}$
	6x8 (No. 67)*	atm. + 100 torr		4.8×10^{-6}
	6x8 (No. 8)*	atm. + 100 torr		n.d.**

* Vibratory compaction

** n.d. not detectable above background after 70 days.

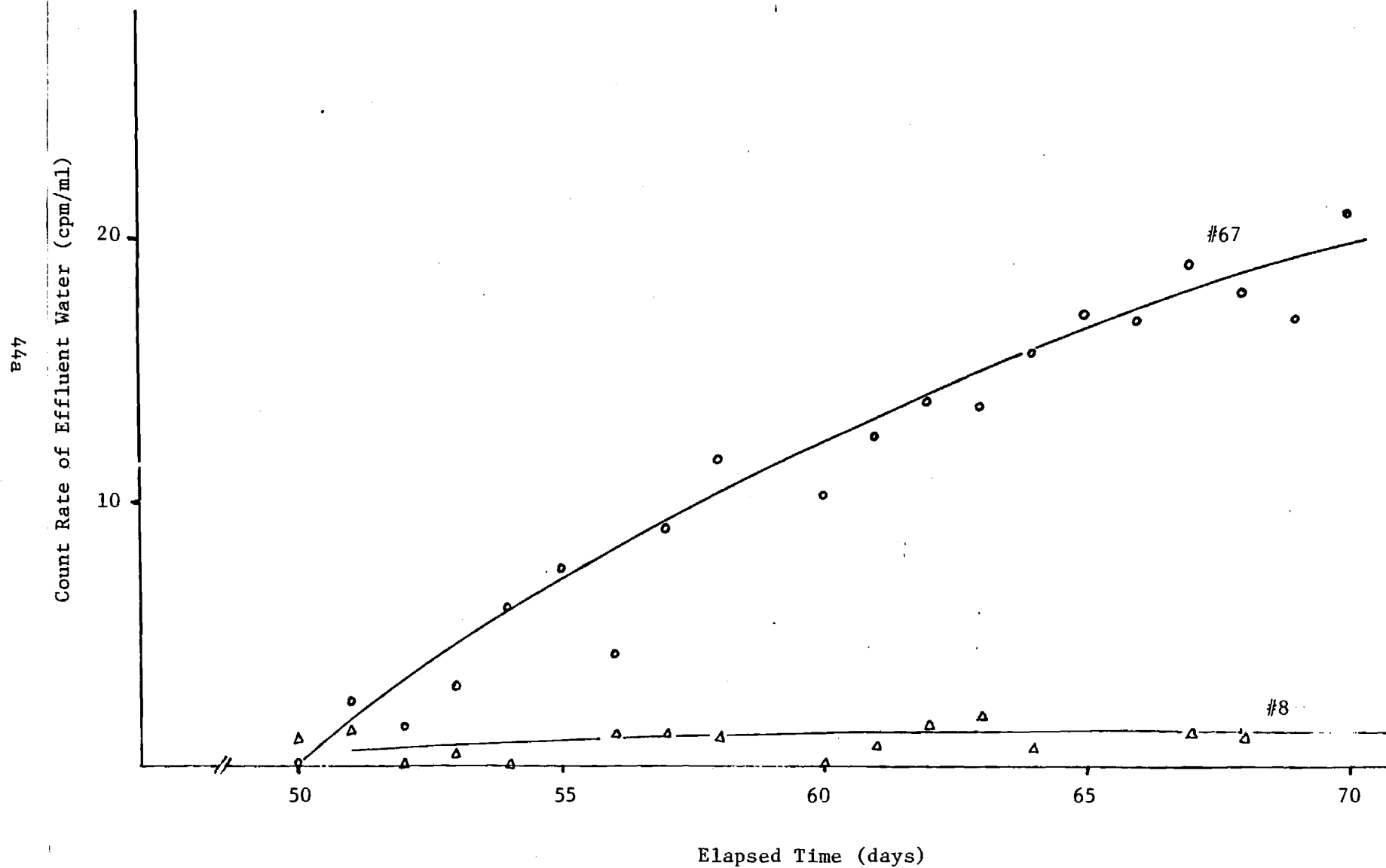


Fig. 20 Water Movement in Compacted Concrete Samples

Table 3 summarizes the numerical results of the migration tests. On the basis of these results the following conclusions may be stated:

- a. In a tritiated water disposal vault, it is reasonable to think that the system would usually be almost wet, about 80% pore saturation, rarely dry.
- b. The rate of wetting, steady state migration rate, and the diffusion coefficient are the critical parameters to analyze the concrete containment.
- c. The rate of wetting was found to be about constant in the experiments, with values between 1 - 4 cm/day, regardless of size of concrete aggregate, and the applied pressure.
- d. The steady-state migration rate was pressure-, thickness-, and aggregate size-dependent.
- e. In calculating the diffusion coefficient by Fick's law, it was found that diffusion may be the major contribution to tritium migration through concrete compared to any other mechanisms, such as exchange, convection, or vapor movement.
- f. Nonuniform porosity and finish give rise to some variations in permeability.
- g. It is suggested that the larger surface area from the use of smaller size of stone produces less permeability compared to the use of a larger size of stone in the aggregate.
- h. It was found, that both migration rate and/or steady-state velocity will reach a low constant rate in the long run, over a few days.
- i. High applied pressure produced a higher infiltration rate in the form of an exponential function.
- j. Vibratory compacting of the concrete mixture before setting reduced permeability significantly and resulted in lower migration rates.

CONCLUSIONS

The work described here has confirmed the relatively rapid diffusion of water through water-saturated concrete, carrying any tritium with it. While most previous work has been done on relatively short concrete samples, the work reported here, on longer and larger samples, has emphasized the importance of thick specimens for fair assessment, to eliminate surface tension effects in near-surface pores. The results obtained agree fairly well with the free aqueous diffusion coefficient of $2 \times 10^{-9} \text{ m}^2/\text{sec}$ quoted by Atkinson and Nickerson and confirmed by them on thin specimens with iodine and cesium tracers. It is evident from Fig. 13 that steady-state flow in thick walls is about an order of magnitude slower than in thin specimens, but even so tritium movement through uncoated concrete walls would be rapid enough, to eliminate the wall as a significant retardation factor.

The movement of water depends critically on the porosity of the material, which is not necessarily uniform between surface and bulk concrete regions. Chino and Kawamura show a significant break in pore volume ratio at a cement-water ratio of 0.35, above which not all the water is transformed into combined water and, instead, remains as saturated water in the solidified cement. At a ratio of 0.46 for water/cement + slag, one would expect some saturated water, quite apart from the infiltrated flow. On the other hand, Chino and Kawamura stress the need to reduce the pore volume ratio to improve cement stability, which is also affected by the formation of ettringite in the presence of sulfate ions.

Our tests have confirmed the importance of the high slag admixture to control pore formation and the significance of a smooth surface finish to minimize surface porosity. Once the concrete is thoroughly wetted, it is unlikely to dry fully again under subsurface structural conditions and the conservative assumption would be to consider the concrete walls saturated. From our results it would appear that there are some benefits from using a slightly smaller stone in the aggregate, but the difference in diffusion rates is not large enough to offset any structural considerations that may dictate the use of #67 stone. In any case, the main problem may be to obtain adequate uniformity and porosity control over the vault concrete as poured.

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APPENDIX

REVIEW OF LITERATURE (Hartman)

Properties of Concrete. A. M. Neville, Pitman Publishing, Great Britain, 1972.

Structure of Hydrated Cement.

- A. Fresh cement paste - plastic network of particles of cement in water.
- B. Hardened paste - hydrates of various compounds, (gel) $\text{Ca}(\text{OH}_2)$, minor components, unhydrated cement, Residue of water-filled spaces or voids.
 - 1. Voids
 - a. capillary pores
 - b. gel pores - interstitial voids in gel matrix
- C. - Hydration products are colloids so surface area of solid phase increases and large amount of free water absorbed on surface. This water used for hydration reactions if no water movement in and out of paste occurs. (self desiccation)

Volume of Products of Hydration:

- 1. Non-evaporable water - 23% of the weight of anhydrous cement (Type II => value may be as low as 18%)
 - a. 0.254 of volume of dry cement
 - b. example
 - 100g hydrated cement sp. gravity = 3.15
 - absolute vol. unhydrated cement $100/3.15 = 31.8 \text{ ml}$
 - non-evaporable - 23% by wt => 23 ml
 - solids = $31.8 \text{ ml} + 0.23(1 - 0.254) \times 100 = 48.9 \text{ ml}$

$$\text{Volume water (gel)} = \frac{W_g}{49.9 + W_g} = \text{porosity} = 0.28$$
$$W_g = 19.0 \text{ ml}$$

Capillary Pores - represent portion of gross volume not filled by products of hydration. This volume decreases with hydration.

- a. porosity(capillary) depends on w/c ratio and hydration.
- b. size - estimated by vapor pressure measurements to be $1.3 \mu\text{m}$.
- c. distributed throughout matrix to form interconnected system responsible for permeability of hardened paste.

Gel Pores - hold large quantities of evaporable water, so gel is porous.

- a. pore - interconnected interstitial spaces between gel particles.
- b. size - $15 - 20 \text{ \AA}$ diameter
- c. occupy 28% of total gel volume

Water held in hydration -

1. Water content depends on ambient humidity.
 - a. free water
 - b. chemically bonded water
 - c. absorbed water - water held by surface forces of gel particles.
 - d. interlayer water of zeolite - held between surfaces of certain planes in crystal.
 - e. lattice water - part of water of crystallization not chemically associated to lattice.

nonevaporable water = 18-28% by weight of anhydrous material.

- Density of water.
- a. nonevaporable = 1.2
 - b. gel 1.1
 - c. free 1.0 g/cm^3

Permeability of Concrete:

- Movement of water through thickness caused by a head of water or by differential humidity or osmotic effects.
- flow similar to flow through any porous body
 - a. paste composed of particles connected over small fraction area and water held within field of force or adsorbed. This water has high viscosity and mobile + takes part in flow.

- Permeability depends on size, distribution, and continuity of pores.
 - a. Gel - porosity of 28% => permeability of 7×10^{-16} m/sec. (due to fine texture).
 - b. Capillary - greater pore size and water flow easier - Cement permeability governed by capillary porosity, 20 - 100 x greater gel.
 - c. Coefficient of permeability versus porosity percent for 0.7 w/c ratio (graph 7.1), order of 10^{-13} m/sec

(Progress of hydration)

<u>Age (Days)</u>	<u>K (m/sec)</u>
fresh	2×10^{-6} m/s
5	4×10^{-10} m/s
6	1×10^{-10}
8	4×10^{-11}
13	5×10^{-12}
24	1×10^{-12}
Ultimate	6×10^{-13}

hydration proceeds, only if water in paste 2 x water combined

Permeability of concretes - (used for demos) Table 7.4

<u>Cement Content</u>		<u>Water/cement</u>	<u>Permeability</u>
Kg/m ³	lb/yd ³	(wt%)	(10^{-12} m/s)
156	263	0.69	8
151	254	0.74	24
138	235	0.75	35
223	376	0.46	28

Bureau of Reclamation work acceptable limit:

1.5×10^{-11} m/sec (Dam materials)

Vapour -

Vapour pressure affects hydration

- a. below 0.8 saturation pressure, degree of hydration is low.
- b. below 0.3 of saturation pressure + negligible

Vapor pressure within cement paste always less than saturated vapor pressure.

Rate of flow for air depends on thickness of concrete and pressure applied; equilibrium rate of flow is reached within several hours.

Magnitude of flow (test on 1:2:6: concrete with w_a/c ratio of 0.62).

<u>Thickness (mm) (in)</u>	<u>Flow Rate</u>	$10^{-9} \text{ m}^3 \text{ per N/m}^2 \text{ h m}^2 = \left(\frac{\text{in}^3 \text{ per lb}}{\text{in}^2 \text{ h ft}^2} \right)$
102 (4)	14.8 (0.58)	
178 (7)	9.5 (0.37)	
203 (8)	7.7 (0.30)	
229 (9)	6.1 (0.24)	

- Increased w_a/c ratio decreases air permeability.
- prolonged curing reduces air permeability, good grade concrete $\sim 300 \text{ kg/m}^3$ impermeable at air pressure of 0.2 MN/m^2 (28 lb/in^2).

Water vapor transmission of concrete generally affected like air.

Reduction in transmission

- due to
1. increased age of concrete
 2. decreased w/c ratio

-Vapor transmission reported $\text{g/m}^2 \text{ day}$ (measured transmission independent of the length of flow path).

-Water vapor permeability decreases on prolonged moist curing.

1. 1-day curing: permeability is twice as large as 3 day curing.
2. 15 times as large after 1 year curing.

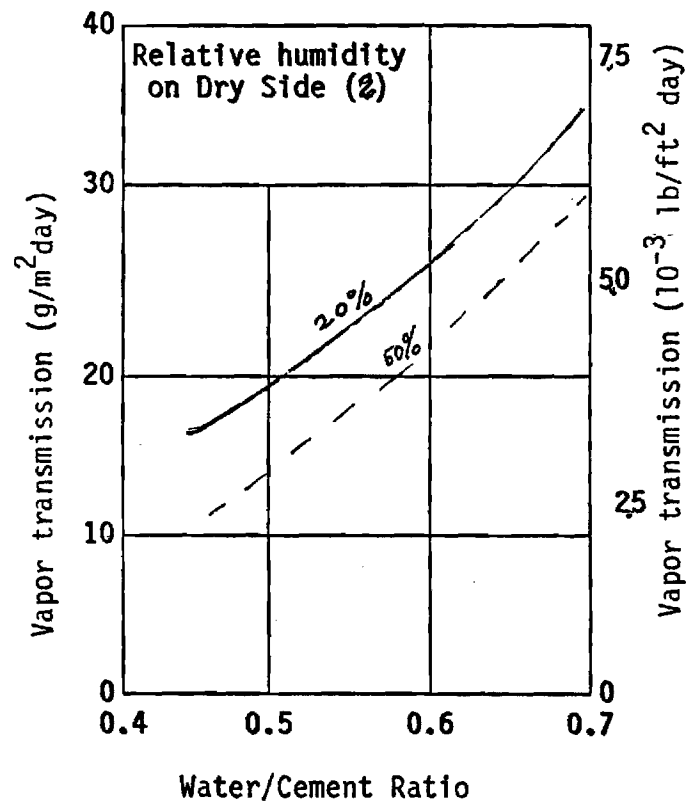
-Vapor unaffected by drying out.

Decrease w/c ratio by 0.8 to 0.4 decreases vapor permeability by 50 to 65%.

Vapor permeability decreases as mean relative humidity increases. This is due to an increase in relative humidity that decreases air-filled pores available for diffusion.

Vapor permeability determined by dry-cup method.

- gravimetric measurement of steady-state vapor transmission through a thickness of concrete under isothermal conditions with zero relative humidity on one side and 50% on the other .
- Virtually all transmission takes place by diffusion and capillary flow absent.



Relation between vapor transmission and w/c ratio for concrete at 23°C (73°F)

Permeability

"Packaging of ^3H contaminated waste" Nuclear Technology 32, 53-59 (1977).
J. J. Danby, Mershad, E.A., Thomasson, W. W.

Collection of Waste: ^3H , ^3H oxides, tritiated pump oil vapors in the ERS (Effluent Removal Storage).

Solidification: maximum weight ratio - 1 part water to 3 parts dry cement plaster mixture.

Organics - 2 parts oil to one part vermiculite or 3 parts "absorbal".

Tritium Content: 70000 Ci max ~ 7g H^3 per 30 gal.

Permeation Test: ^3H cement in polyethylene bottle (0.155 cm thick)

- immerse in plastic container of measured volume water
- liquid water or vapor exposed to surface area A and wall thickness L.

$$\text{Rate (HTO)} = K \frac{a \times A}{V \times L}$$

a = H^3 activity/mol
k = permeability of water in material
f = molar fraction of HTO

$$R_{\text{H}_2\text{O}} = K \frac{S}{P_{\text{H}_2\text{O}}} \cdot A/L$$

$$= \frac{n_{\text{HTO}}}{n_{\text{H}_2\text{O}}} = \frac{a}{a_m} \times \frac{V_m}{v}$$

$$R_{\text{HTO}} = f \times R_{\text{H}_2\text{O}}$$

m = Moles, v = volume
 V_m = molar water volume l/mol
 a_m = molar activity

Permeability constant for HTO through Polystyrene

<u>Material</u>	<u>R_{HTO} (Ci/month)</u>	<u>$A(\text{cm}^2)$</u>	<u>$K = \text{Ci-cm/cm}^2\text{-Ci/l month}$</u>
Vermiculite	0.30	375	7.08×10^{-8}
Cement plaster	0.21	375	4.96×10^{-8}
Water	0.11	375	2.6×10^{-8}

Conclusions:

Amount ^3H released each year to ground water should not exceed 0.0001% of total ^3H in container.

Yearly release decreases 5.5% each year due to decay of ^3H

Projected ^3H release of burial after 85 yr would be 0.002% total ^3H in package or ~ 1.4 Ci of 70,000 Ci.

Leaching by Diffusion

"Leaching Behavior of Cesium-137 in Cement-Waste Composite". Health Physics Journal 32 (June), 529-534 (1977). Matsuzura, Moriyama, Wadachi, Ito.

Assessment of leaching of Cs^{137} from Composite Waste into surrounding fluid environment.

- leach process consist of physicochemical transport phenomena with diffusion playing important role.
- procedure used matrix cement composite containing a radionuclide which disperses uniformly and a surrounding liquid phase which is assumed to be homogeneous composition.

$$f \text{ (fractural leaching)} = \frac{a}{A} = \frac{2S}{V} \frac{\sqrt{Dt}}{\sqrt{\pi}} \quad D = \frac{\pi m^2 v^2}{4S} \quad m = \text{slope (F vs } \sqrt{t} \text{)}$$

Phases of leaching - initial and later stage L_i and L_1

- both diffusion coefficients increase with w_a/c ratio
- dependence coincides with dependence of surface area and porosity on w_a/c ratio.
- water permeability determined by pore structure of matrix: porosity, surface area, pore distribution of various volumes and surface.
- pore structure depends on ratio of water to cement and both porosity and surface area increase with ratio.

Penetration of Water

- Water penetrates through pores that extend into cement paste and throughout matrix.
- This important for leaching of Cs^{137} and other easily soluble and freely mobile in water components.
- water penetrates through pores and radionuclides (Cs^{137} or 3H) incorporated in paste may come into contact with penetrating water and be dissolved.
- This enables radionuclide to leach out.
- Conclude: (1) leaching increases with increased w_a/c ratio
(2) total volume of pores in cement increases so radionuclide is allowed to diffuse into external fluid producing a faster leach rate.

(Tables of leach rates) page 530.

Variable Leach Rate (initial vs later)

$L_i > L_1$

- Early Stages: exposed area of cement limited to surface and/or an extremely thin layer.
- Rate of penetration of water may be more rapid with that of deeper layers. As leaching time continues, it gradually slows down as exposed layer becomes thicker.

Leaching by Diffusion

"Leaching Behavior of Tritium From a Hardened Cement Paste". Annals of Nuclear Energy, 6, 417-423, (1979).

Authors: Matsuzūra, Nobaru Mariyama, Akihiko Ito.

Leachability - water not fixed chemically, is held physically as gel or capillary water in pore structure that extends through hardened cement paste. This water can exchange with external sources of water that penetrates into pore structure and diffuses through material.

Amount leached: determined by or is function of

1. Water-cement weight ratio (wa/c),
2. Temperature of leachant
3. Curing time

Leach Data: IAEA methods

$$f = 2 S/v \sqrt{\frac{Dt}{\pi}}$$

f = cumulative leaching fraction at t(days)

D = cm²/day, diffusion coefficient

v = volume, cm³

S = surface area, cm²

$$D = \frac{\pi m^2 v^2}{4 S^2}$$

Diffusion coefficient - obtained from slope of relation of f and \sqrt{t}

$$\Rightarrow f = m \sqrt{t}$$

Leaching Process: 2 stage procedure (curve page 418)

A. initial process

$$f_1 = m_1 \sqrt{t}$$

Later Stage: $f_1 = m \sqrt{t} + a$ (a intercept)

Leaching Coefficient: L

$$L = \frac{\pi m^2 v^2}{4 S^2}$$

Table of values page 419 for various samples by water-cement weight ratio and curing time.

Results:

1. Slag cement - low hydration temperature, high resistance to chemicals and low permeability to water.
2. Hydration reactions of cement proceed slowly over long periods of time. Pore structure of hardened cement paste becomes finer gradually.
3. Leaching process of ^3H governed by permeability of water in and through pore structure of cement paste.

Pore Structure - depends on wt ratio of water to cement.

- penetration of water into paste through pore structure that extends through whole body of matrix and plays important role for (H^3HO) which is freely mobile in water.
- Slag cements => keeps relatively fine pore structure with relatively high leach resistance.

Reduce ^3H leachability -

1. Lower w_a/c ratio - reduces workability
2. Increase curing time (Portland and slag cement).
 - hydration of cement causes pore structure in paste to become gradually finer.

Leaching Process:

- A. diffusion of ^3H that exist in matrix as a gel or capillary water.
- B. Dissolution of cement paste containing ^3H water as hydrated water.

- velocity of diffusion: concentration gradient dependent.
 - a. diffusion depends on leachant makeup ($\text{Ca}(\text{OH})_2$ vs H_2O)

Temperature Effects:

1. leachability increases with leachant temperature
 - diffusion kinetics known to have lower activation kinetics than chemically controlled kinetics
 - * -leaching process of ^3H water controlled by diffusion

Values:

	<u>Cement</u>	<u>W_a/C</u>	<u>Curing time (d)</u>		<u>L_i (cm²/day)</u>	<u>L_i (cm²/day)</u>
1.	Portland	0.3	7	Deionized	2.22×10^{-3}	5.10×10^{-4}
2.	Portland	0.33	7	Water	2.79×10^{-3}	7.22×10^{-4}
3.	Portland	0.36	7		3.66×10^{-3}	1.12×10^{-3}
4.	Portland	0.33	7		2.13×10^{-3}	4.96×10^{-4}
5.	Portland	0.36	7		2.54×10^{-3}	6.01×10^{-4}
6.	Portland	0.39	7		3.05×10^{-3}	8.22×10^{-4}
7.	Portland	0.30	28		1.25×10^{-3}	3.54×10^{-4}
8.	Portland	0.30	50		9.84×10^{-4}	2.82×10^{-4}
9.	Portland	0.30	80		1.01×10^{-3}	3.03×10^{-4}
10.	Portland	0.30	7	Salt Water	8.64×10^{-4}	1.85×10^{-4}

Polymer Impregnated Concretes

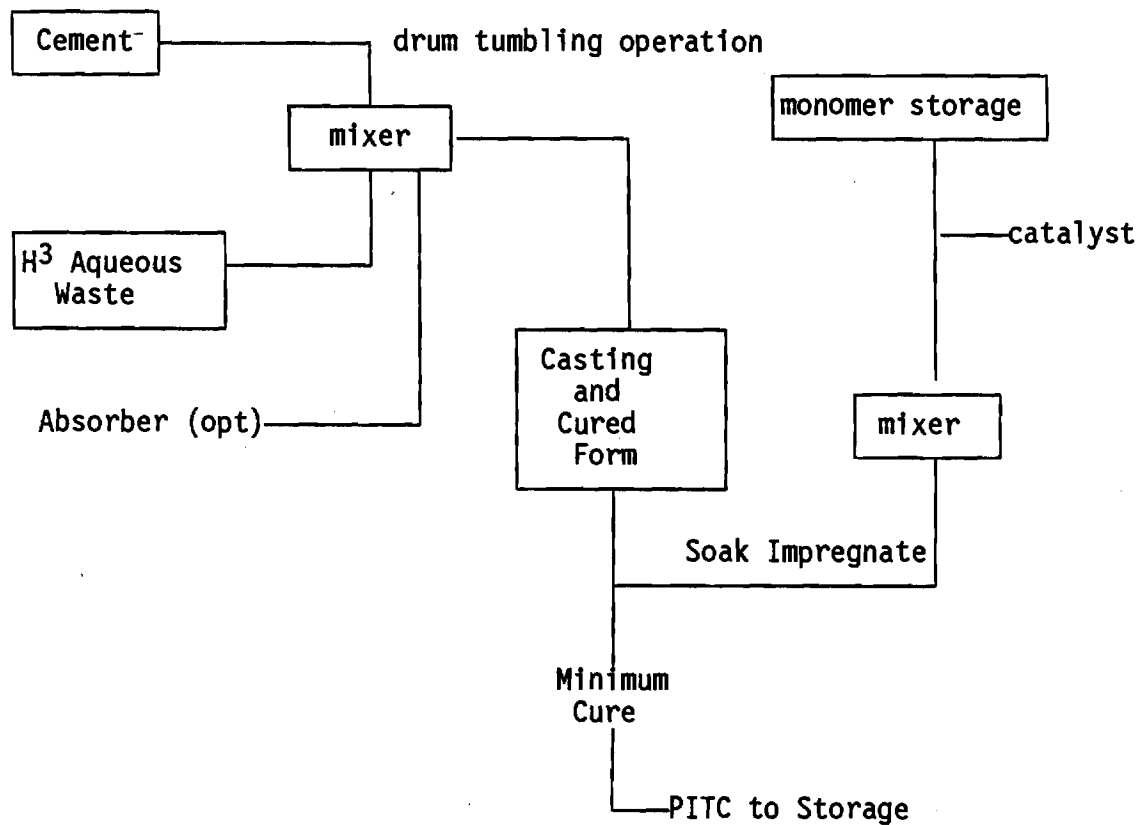
(BNL - 20898) Fixation of Aqueous Tritiated Waste in Polymer Impregnation Concrete and Polyacetylene.

H³ waste used to hydrate hydraulic cement producing concrete that contains network of interconnected porosity. Product is subject to water intrusion and H³ loss by leaching and exchange. Impregnate porosity with styrene monomers which is the polymerized producing essentially impermeable concrete while improving strength, durability, and resistance to chemical attack.

-H³ bulk release rate as low as 1.68×10^{-4} g/cm²-day
-Absorbent additives incorporated to increase specific H³ waste loading of concrete. Composite 5.8 - 8.3 liters per cf.

H³ fixed as polymeric form of polyacetylene -
50 Atomic % tritium is essentially non-leachable, insoluble, thermally stable to 325°C, chemically inert.

-bulk leaching rate 1.8×10^{-8} g/cm²-day.
-Hydrolysis by Co⁶⁰γ: - G value for H product 0.15 molecule/100eV.
- incorporate as aggregate in concrete, polymer concrete, PITC to form monolithic solid.



water/cement ratio: ~ 0.20

Leachability: IAEA Standard Leach Test

<u>Specimen</u>	<u>Cement</u>	<u>Silica gel</u>	<u>H₂O</u>	<u>W/C ratio</u>	<u>W/Absorbed</u>
Laminated H ³ concrete	84.7	-	15.3	0.18	-
Lumetic PITC	84.7	-	15.3	0.18	-
Portland Type III	84.7	-	15.3	0.18	-
Lumetic silica gel	40.4	36.8	22.8	0.18	0.40
Portland Type III (S.G. PITC)	40.4	36.8	22.8	0.18	0.40

Release leach rate (Bulk) L_B

$$L_B = F_i \times \frac{d \times v}{s \times t}$$

F_i = fract. release of ith specimen

d = composite density g/cm³

v = composite vol. cm³

s = surface area cm²

t = leach time, days

<u>Specimen</u> (100 μCi H ³)	<u>Surface area</u>	<u>Mass</u>	<u>Time</u>	<u>Fract/day</u> <u>FR</u>	<u>g/cm²/day</u> <u>=></u> <u>BR</u>
L. H ³ C	248.8	650	10	3.59x10 ⁻²	9.33x10 ⁻²
P.III H ³	336.5	456.7	10	6.56x10 ⁻²	1.11x10 ⁻¹
Lum PITC	298.6	693.0	10	7.25x10 ⁻⁵	1.68x10 ⁻⁴
PIII PITC	282.2	673.4	10	1.01x10 ⁻⁴	2.41x10 ⁻⁴

Polyacetylene Form: 2.95 gm P.A. w/ S.A of 0.332 μCi/g.
bulk release rate 1.8 x 10⁻⁸ g/cm² - day

Polymer Impregnated Concrete

(BNL - 50625) Progress Report 9

Lysimeter testing on polymer impregnated tritiated concrete at SRP. 31 weeks, constant ave. H^3 fraction release rate of 1.6×10^{-6} per day was reached in percolated water with no measurable release into air. Long-term projection that complete H^3 release from PITC would be 2,370 yrs and max. fraction of the initially contained H^3 present in environment would be 2.73×10^{-3} after 17.7 yrs. Static leaching in distilled water - 295 days constant H^3 fraction release rate 1.89×10^{-5} day⁻¹.

Lysimeter Testing:

- Specimen one to ten curies of H^3 detectable using lysimeter.
 - Each specimen 10 Ci - five gallon screw top (0.67ft³) polyethylene carboys.
 - dough top mixer (Blakeslee model B-20), water to cement ratio of 0.22 produced similar density to end-over-end tumbling.
 - polymer loading in homogeneous cement casks using soak impregnation.
 - water necessary to H_2O /cement ratio 0.22 => 2 ml tritiated H_2O with S.A = 5 Ci/ml.
- added to water to make 10 Ci. Water added to Portland Type III cement, mixed till uniform.

<u>Specimen</u>	<u>Cement Wt%</u>	<u>Water %</u>	<u>HTO μ/ft³</u>
1	82	18	7.44
2	82	18	7.47
3	82	18	7.47
4	82	18	7.47

Figures on cumulative HTO (μ Ci) with time since burial.

Release: SE lysimeter 2.83 mCi (31 wks)
NW " 0.0786 mCi
Average release 1.052 mCi => percolated fraction 1.05×10^{-4}
 1.16×10^{-6} per day after 12 weeks
Cumulative fraction (release/time) x (V/s) in trusion factor
 $Vol/Surf. area = 5.26 \times 10^{-6}$ cm/day.

Static Leach Testing: Leach rate in distilled water (w/o container).

- immerse in 40 liter distilled H₂O. All surfaces exposed to leachants.
 - = 8.61×10^{-5} cm/day cumulative release fraction.
 - = complete release 145 yrs.

Preparation of PITC Injector Method.

- + injector to distribute H³ in dry cement
- + add H³ till reaches outer surface

Diffusion

Reference

"Characterization of the Class B Stable Radioactive Waste Packages of the New England Nuclear Corporation". E. P. Gause, E. Veakis, J. Smalley. Brookhaven National Laboratory (NUREG/CR-3018, BNL - NUREG - 51607), 1983.

Portland Type Concrete

gel pores 15 to 20 Å diameter (Angstroms)
Capillary Cavities - Average 5000 Å

Mean Free Path Hydrogen molecule (25°C and 1 atm) - 1200 Å
results from an existing pressure gradient

-Poiseuille Flow predominates in concrete - flow of hydrogen through porous media inversely proportional to viscosity of gas. Gas diffusion through concrete is less than a day.

Tritiated liquid - moves through concrete by diffusion if concrete pores full of liquid and is a slow process. Diffusion through gas phase greater.
long term - Diffusion through concrete depends upon containment barrier.

Short term containment (Low Activity)

-gaseous waste package - transport mechanism is diffusion since no pressure gradient exists to drive Poiseuille Flow.

-Gas diffusion coefficient approximate value $1 \times 10^{-2} \text{ cm}^2/\text{s}$
-allows for very rapid transport of tritium gas through cement overpack. Visible on surface within a day.

High Activity - (Solvents)

- behavior similar for tritiated gaseous vapor + Solvent transported by gas phase diffusion
- very small fraction of total tritium appears rapidly as gas at inner surface of containment.
- transport of tritiated liquid through concrete occurs via diffusion.
- Diffusion coefficient of measured tritiated water (HTO) in concrete ranges from 1×10^{-8} to $1 \times 10^{-9} \text{ cm}^2/\text{s}$ second.
- liquid transport of tritiated solvent slow compared to gaseous transport.